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Quantum Mechanics

A3 Lecture Notes

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ABSTRACT:

This is an introductory course on quantum mechanics. There are many textbooks on quantum mechanics and I encourage you to find one that fits you. Here I mention two specifically

- Binney and Skinner, "*The Physics of Quantum Mechanics*"

James Binney lectured this course for many years and this book is the result. As the book developed around the A3 course (and the syllabus is broadly unchanged), you may find it the best single book to accompany the course. The book also explicitly contains many of the problems that will crop up on the problem sheets.

- P. A. M. Dirac, "*The Principles of Quantum Mechanics*"

This is a truly classic book where you get a strong sense of the personality of one of the founders of quantum mechanics (Like the Feynman lectures, although with an entirely orthogonal style). The approach is not for everyone but it presents the bra-ket approach to quantum mechanics with maximal clarity and minimal frills.

I also recommend the lecture notes of the three previous lecturers, Fabian Essler, Stephen Blundell and James Binney. These are linked via the course webpage. https://www-thphys.physics.ox.ac.uk/people/JosephConlon/A3Quantum.html

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Acknowledgements

Thanks to all the previous lecturers of A3 Quantum Mechanics, whose lecture notes and problem sheets I have frequently referred to while writing this course.

Thanks also to the many New College undergraduates over the years to whom I have had the privilege of giving Quantum Mechanics tutorials. You can only once learn quantum mechanics for the first time. But the next best thing is helping others learn it.

1. Basic Concepts

Plato. Aristotle. Pāṇini. Li Bai. Leonardo da Vinci. Shakespeare. Isaac Newton. Émilie du Châtelet. Not one of these ever got a glimpse of quantum mechanics. However prodigious their intellectual talents were, you, although still children, are more fortunate than any of them because you get to become scientific adults and learn quantum mechanics, the deepest and most important scientific discovery of the 20th century.

As long, that is, you attend the lectures and do the problem sheets. Relying on school physics or old intuition will get you nowhere here – quantum mechanics has to be learned. However bright you are, you cannot lock yourself in a room and think yourself into finding out the principles of quantum mechanics.

Hwaet. Let us begin. I start with an important and simple point which students sometimes do not fully absorb as part of their mental outlook. That is,

The world is quantum, not classical. Therefore, there is no such thing as quantisation.

Although the expression 'quantisation' is commonly used, and indeed we will also use it, the actual laws of nature are not classical. Quantum mechanics is not some extra level of finesse and detail we apply to classical theories. Rather, the world is, always was and always shall be quantum *in saecula saeculorum.* What we call 'classical physics', and the laws we use to describe classical physics, emerges as a certain limit and approximation of this quantum world, but has no independent existence. Properly understood, *classicalisation* is a feature of the world – where classical physics can be used in certain circumstances to approximate the quantum world – but not *quantisation.*

This also means that if you ask why some of the fundamental postulates of quantum mechanics are true, the answer may be no more and no less than simply 'because this is the way the world is, supported by plentiful experimental evidence'. So far as we know (and certainly from the perspective of this course), there is no deeper framework from which the fundamental postulates and equations of quantum mechanics arise as subsidiary deductions.

Like it or loathe it, appealing or off-putting, quantum mechanics is the way the world is. The purpose of these lectures is to teach you this way; and then in your own time you can reflect on and address the question of why reality takes this form.

1.1 Probabilities and Amplitudes

The business end of physics involves predictions. Suppose we start with a known physical configuration. What happens when we do a measurement on it? What happens when we let the system evolve in time, and then do a measurement? What will we observe? What results will we get from an experiment?

Let us be slightly more precise in our examples. If we fire a single photon of fixed frequency f towards a slit of width L – or two slits, or some complicated combination of slits – leading to a screen a certain distance D beyond the slits, what is the probability the photon will be detected *here* or *there* on the screen?

Another example. Suppose we accelerate two protons at the CERN Large Hadron Collider and collide them into each other, what is the probability that they will produce a physical Higgs boson?

Another example. Suppose a highly excited atom in a distant galaxy decays to produce an emission line, what are the probabilities for each decay mode? What spectrum of emission lines will we observe?

Probabilities (which are necessarily real numbers) are at the heart of all prediction. However, one of the first and most important lessons in quantum mechanics is that these real numbers originate from complex ones called *amplitudes*. In particular, the probabilities that appear in all predictions for measurements are computed as the complex square of amplitudes. That is,

$$\mathrm{Prob} = |\mathcal{A}|^2 \equiv \mathcal{A}\mathcal{A}^*. \tag{1.1}$$

Here $\mathcal{A}$ is a complex amplitude and Prob is the physical probability that we want to compute.

Why is this significant? In classical physics, we combine probabilities. If there are two separate disjoint ways a single process can happen (call these 1 and 2), then

$$\mathrm{Prob}_{event} = \mathrm{Prob}_1 + \mathrm{Prob}_2. \tag{1.2}$$

However, in quantum mechanics this is *not* the case. If there are multiple amplitudes contributing to a single process, then *in quantum mechanics we add the amplitudes not the probabilities*. This point is absolutely critical to how quantum mechanics operates and is key to a lot of the non-intuitive behaviour of quantum mechanics.

In quantum mechanics, we combine amplitudes first.

$$\mathcal{A} = \mathcal{A}_1 + \mathcal{A}_2. \tag{1.3}$$

and it is the *combined amplitude* which is turned into a probability.

$$\text{Prob} = |\mathcal{A}_1 + \mathcal{A}_2|^2. \tag{1.4}$$

As is familiar from the behaviour of constructive and destructive interference from waves,

$$|\mathcal{A}_1|^2 + |\mathcal{A}_2|^2 \neq |\mathcal{A}_1 + \mathcal{A}_2|^2. \tag{1.5}$$

While quantum probabilities are strange, they are not infinitely strange. In particular, they do add up to one in the completely conventional sense. Suppose we a measure of some quantity x, which can either take discrete values x_1, x_2, x_3, $\ldots x_n$ or continuous values $x \in \mathbb{R}$, then we have either

$$\sum_i \text{Prob}(x_i) = 1 \tag{1.6}$$

or

$$\int dx\, \text{Prob}(x) = 1 \tag{1.7}$$

depending on whether we are in the discrete or continuous case.

We will now see an application of such quantum amplitudes in the two-slit experiment.

1.2 Formulations of Quantum Mechanics (off-syllabus)

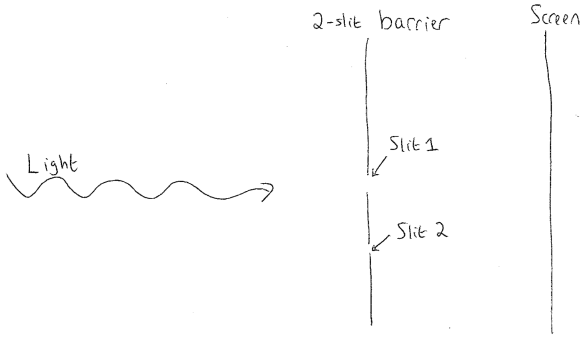
This subsection is not strictly on-syllabus, but it is included as deep background as you may find it helpful in contextualising the two-slit experiment. When developing the formalism of quantum mechanics, there are two ultimately equivalent approaches – meta-approaches, as it were. The first, and less general, is that of canonical quantisation (the path trodden by Heisenberg, Schrödinger, Dirac etc which we will follow for the rest of the course). The second – more subtle but more general – is the Feynman path integral approach. If you pursue the subject to more advanced levels, you will find the latter remains applicable in certain complex problems (for example, formulating the quantum theory of the strong and weak forces of the Standard Model) where the canonical approach breaks down.

For good reasons, it is a universal pedagogical tradition that introductory courses on quantum mechanics follows the canonical approach and ignore the path integral approach – *except* in the very first and simplest example of a quantum system, the two-slit experiment, which is implicitly presented using the path-integral approach.

I shall not break with this tradition, but I note (and encourage you to note) that the structure of how we think about quantum systems will look different in the 2-slit experiment compared to all later parts of the course.

1.3 The Two-Slit Experiment

The double-slit experiment is one of the oldest quantum-mechanical examples. We suppose we have a source of light emitting towards a screen, with a barrier consisting of two slits inbetween. What is the pattern of light found on the screen on the far side?



Before answering, we can sharpen this problem. Instead of talking about some general source of light, firing out vast numbers of photons, we can gradually reduce and reduce and reduce the intensity of the light so that it can no longer possibly be viewed as a continuous wave, but only as a set of individual particles (photons, in this case). Given the expression for the energy of a photon,

$$E = hf \tag{1.8}$$

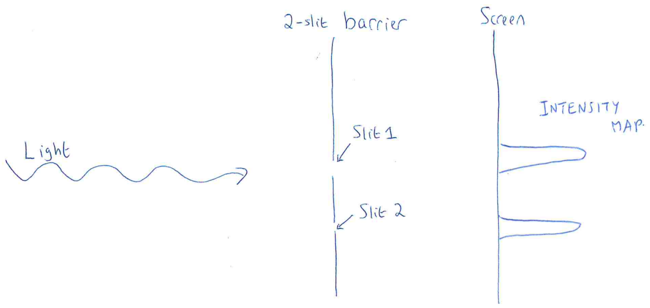
once the power output of the source is less than one photon per second, there is no way we can view the light coming from the source as a classical wave. The emitted light can now only be described in the form of individual quantised particles: photons.

However, even when emitting single particles, by waiting a long time we can gradually build up an arriving intensity pattern at the distant screen. What does this look like? What should it look like?

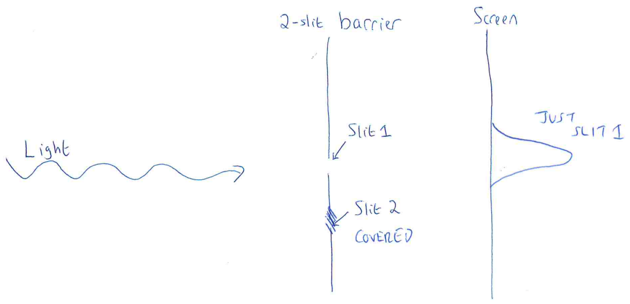
First, what is the classical expectation?

In the classical picture, the source is emitting particles. Each particle is emitted from a definite location (the light source) and with a definite momentum and direction of travel. They head out along a straight line and, barring any rare events such as colliding with the sides of the slits, will continue on that straight line.

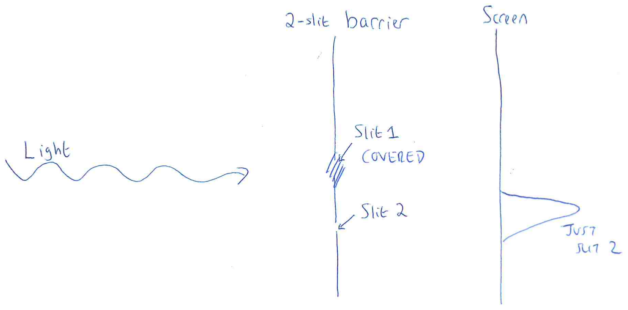
There are two slits. Classical particles that reach the screen can go through *either* slit A *or* through slit B (those that bounce off the barrier and never reach the screen do not matter for this purpose). This implies that classical particles should produce an intensity map on the far screen that looks somewhat like



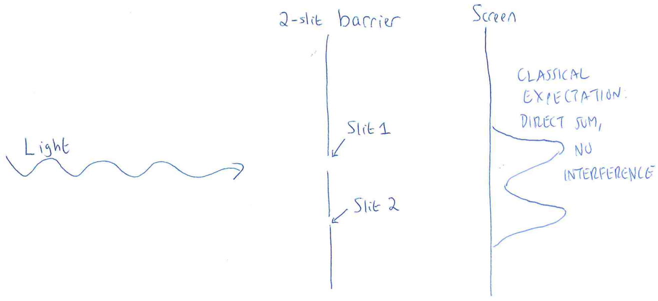
Let us even suppose, however, that classical particles have a bit more weirdness, a bit more fuzz, than this. Suppose that they are able to spread out a bit on passing through slit A or slit B, and can exhibit some wavelike behaviour. For example, suppose that if we only have slit A present then the resulting distribution of intensity is something like



whereas if we only pass through slit B, then the resulting distribution of intensity now looks like



In classical physics, particles must pass through *either* slit A *or* slit B. It is then 'obvious' that the intensity distribution in the presence of both slits will be the direct sum of the two individual intensity distributions



Unfortunately, this 'obvious' conclusion is false.

It is false because quantum mechanics does not involve the addition of probabilities. Instead, it add amplitudes, which then subsequently turn into probabilities. In the quantum world, for any point x on the screen, there is an amplitude for the path heading via slit A: $\mathcal{A}_A$ and a separate amplitude for the path heading via slit B: $\mathcal{A}_B$.

The intensity at a point x on the screen is then

$$\begin{aligned} I_x &= |\mathcal{A}(x)_A + \mathcal{A}(x)_B|^2 && (1.9)\\ &= |\mathcal{A}(x)_A|^2 + |\mathcal{A}(x)_B|^2 + (\mathcal{A}(x)_A^*\mathcal{A}(x)_B + \mathcal{A}(x)_A\mathcal{A}(x)_B^*) && (1.10)\\ &\neq |\mathcal{A}(x)_A|^2 + |\mathcal{A}(x)_B|^2 && (1.11) \end{aligned}$$

and, trivial though it might seem, in that last $\neq$ sign lies one of the deepest features of quantum mechanics, the notion of amplitudes and quantum interference.

There is an amplitude to reach point x passing through slit A. There is an amplitude to reach point x passing through slit B. The amplitudes for the two different paths are added and these can interfere either constructively or destructively.

The above is all true and correct quantum mechanics – however, it also fits most easily into the Feynman path integral way approach to quantum mechanics, where the amplitude for any process is obtained by adding up amplitudes for all possible ways for that process to occur (here, by going through either slit A or slit B). Having noted that, we shall now develop the more traditional route into quantum mechanics.

2. Quantum States, Dirac Notation and Operators

2.1 Dirac Notation

Introductory quantum mechanics textbooks have various choices for how they approach quantum mechanics. Some start with wavefunctions, as per Schrödinger. The wavefunction approach is developed around the quantum mechanics of particles (specifically, electrons in atoms) and gives an intuitive sense of where particles are likely to be found in atomic orbitals. If you read encountered popular presentations of quantum mechanics, it is likely that these involve wavefunctions.

But this is Oxford and you are here to learn the subject properly. We therefore go via a different route, involving Dirac notation from the outset. We do this because Dirac notation, although at first seem odd, is the best (and right) way to understand quantum mechanics; it works for all quantum systems in a way that the wavefunction formalism does not and so we choose to grasp this nettle right at the beginning.[1]

At first, the Dirac notation, with its language of bras and kets, may seem slightly strange. If it does, then please persevere with it. Dirac notation is absolutely the best way to understand quantum mechanics and think about it. Furthermore, wavefunctions only apply when thinking about spatial positions of particles. In contrast, Dirac notation applies just as easily for quantum systems with (say) only 2 possible states, the most notable example of which are spin systems (as spin-(1/2) fermions come with two spin states). It also provides a clear conceptual basis for thinking about the subject.

Mathematically, Dirac notation involves the description of quantum systems as complex linear vector spaces, i.e. Hilbert spaces. In that respect, the Dirac notation can be viewed simply as a convenient physics notation for about elements of, and operators on, complex vector spaces.

The basic building block of Dirac notation is the ket:

$$|\psi\rangle \tag{2.1}$$

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[1] You may find some of the history of this helpful. When quantum mechanics was first discovered, there were two frameworks for describing atomic orbitals: the Schrödinger approach using wavefunctions and Heisenberg's matrix mechanics using infinite-dimensional matrices. These gave exactly the same answers, but also seemed wildly different from each other. Dirac's first big contribution to the subject was to construct a much more general formalism (this is the bra/ket language) and show that the Schrödinger and Heisenberg approaches were both simply special cases of this written out in different ways, and so had to give the same answer. Furthermore, Dirac's formalism could also directly apply for quantum systems that looked nothing like electrons in atomic orbitals.

The ket represents a quantum state (in physics language) or an element of a complex vector space (in maths language). The quantum state is the state of the system. Those are four soft words, but they contain enormous implications. 'State of the system' – that means we know everything about the system, we know precisely what its configuration is at that particular time.

The ket $|\psi\rangle$ contains complete information about the current state of a quantum system; there are no 'extra' degrees of freedom beyond those described by the ket.

Put in more mathematical language, the kets $|\psi\rangle$ are elements of a complex vector space V. The elements of V define the possible quantum states of the system.

For the moment, we are going to stick to finite-dimensional vector spaces: this has all the key physics, and it avoids several subtleties that we can then address later. In this case, we can construct a complete basis of kets,

$$|\psi_i\rangle \tag{2.2}$$

such that *any* element of the vector space can be written as a complex linear combination of the basis kets,

$$|\phi\rangle = \sum_i \lambda_i |\psi_i\rangle \tag{2.3}$$

for complex coefficients λ_i.

The vector space also contains a notion of a scalar product, or a way of measuring the overlap of two states. We write this scalar product between two kets $|\psi\rangle$ and $|\phi\rangle$ as

$$|\psi\rangle \cdot |\phi\rangle = \langle\psi|\phi\rangle \tag{2.4}$$

The physical interpretation of this is: suppose the quantum system is in state $|\phi\rangle$. If we do a measurement, what is the quantum amplitude for it to be found in state $|\psi\rangle$?

As with all other vector spaces, it is also generally sensible to work with *orthonormal* complete sets of basis vectors, namely a set $|\psi_i\rangle$ with the properties that

- $\langle\psi_i|\psi_j\rangle = \delta_{ij}$
- Any ket $|\phi\rangle$ can be written as a linear combination of the basis kets $|\psi_i\rangle$,

  $$|\phi\rangle = \sum_i \lambda_i |\psi_i\rangle \tag{2.5}$$

  for some complex λ_i

The notion of the scalar product allows to define the notion of *bra* states (mathematically, these are elements of the dual vector space V^* defined by linear maps from V to $\mathbb{C}$) and to give a natural basis of the dual vector space.

How do we do this?

- First, construct an orthonormal basis $|\psi_i\rangle$ of kets of the vector space V.
- Given the orthonormal basis $|\psi_i\rangle$, we can construct the corresponding *bra* states $\langle\psi_n| \in V^*$ by
$$\langle\psi_j|\psi_k\rangle = \delta_{jk} \tag{2.6}$$
- We can now extend to general states $|\psi\rangle = \sum_i \lambda_i|\psi_i\rangle$ by defining the bra corresponding bra state (note the complex conjugate)
$$\langle\psi| = \sum_i \lambda_i^* \langle\psi_i| \tag{2.7}$$

'Bra' and 'ket' are so-called because together they form a bra(c)ket. This language is now completely standard; blame (or credit) Dirac.

So the dual space also has a similar complete basis of bra states, $\langle\psi_i|$ which carry exactly the same information as the kets (and, because students often gets this wrong, I reiterate that the dual of $\lambda|\psi\rangle$ is $\langle\psi|\lambda^*$). A general bra $\langle\phi|$ can be written as a linear combination of basis states,
$$\langle\psi| = \sum_i \langle\psi_i|\lambda_i^*. \tag{2.8}$$

Note that if we have two states $|\phi\rangle$ and $|\chi\rangle$, expanded in terms of the basis states $|\psi_i\rangle$,
$$|\phi\rangle = \sum_i \lambda_i|\psi_i\rangle, \tag{2.9}$$

$$|\chi\rangle = \sum_i \mu_i|\psi_i\rangle, \tag{2.10}$$

then it follows that
$$\langle\phi|\chi\rangle = \left(\langle\chi|\phi\rangle\right)^*, \tag{2.11}$$

which is indeed how the scalar product of a complex vector space is meant to behave.

In precise analogy to the dot product of vectors with their dual vector,

$$\begin{pmatrix} a^* & b^* & c^* \end{pmatrix} \cdot \begin{pmatrix} a \\ b \\ c \end{pmatrix} = |a|^2 + |b|^2 + |c|^2 \tag{2.12}$$

the bra and ket can be combined to give a measure of the size of the state.

$$\Big| |\psi\rangle \Big|^2 = \langle\psi|\psi\rangle. \tag{2.13}$$

Normally, physical states ar chosen to have unit normalisation so that

$$\langle\psi|\psi\rangle = 1. \tag{2.14}$$

The language of complex vector spaces, scalar products between states and the norms of states is the mathematical backdrop of quantum mechanics. There is – as yet – very little physics in the above. Rather, we are setting up the right mathematical language on which to overlay the physics of quantum mechanics.

You may be surprised to realise how how strange some of these mathematical concepts – linear algebra and the like – appeared to the original developers of quantum mechanics. Unlike you, they weren't taught linear algebra in the first year of undergraduate studies because it would be key for the quantum lectures in the second year.

Here is Max Born reflecting on the origin of quantum mechanics

> By observation of known examples solved by guess-work [Heisenberg] found this rule and applied it successfully to simple examples....
>
> I could not take my mind off Heisenerg's multiplication rule, and after a week of intensive thought and trial I suddenly remembered an algebraic theory I had learned from my teacher, Professor Rosanes in Breslau. Such square arrays are well known to mathematicians and, in conjunction with a specific rule for multiplication, are called matrices.

Advanced mathematics!

It is important to appreciate that this picture of complex vector spaces applies to *every single* quantum systems. Of course, the nature and dimensionality of the actual vector space (the 'space of states') will differ between different physical systems. But the underlying mathematical framework remains the same: a complex vector space with a scalar product (a Hilbert space).

Here are some examples of such state space (i.e. complex vector spaces):

- A two-state system, often used for spin systems of an electron (or another similar fermion), where the two states are *up* and *down* spin, $|\uparrow\rangle$ and $|\downarrow\rangle$
- An n-state system, which often appears in general angular momentum problems or in other cases where we can truncate to a finite number of states: $|1\rangle, |2\rangle, |3\rangle, \ldots |n\rangle$
- An infinite *but countable* set of states, which can be given an integer ordering $|1\rangle, |2\rangle, |3\rangle, \ldots$. This appears in both the harmonic oscillator and the hydrogen atom, and also in many other systems of a particle bound in a potential well.
- An infinite *but uncountable* set of states, which are labelled by a continuous *real* parameter (e.g. $x \in \mathbb{R}$). This is common in systems of *unbound* particles, the simplest of which is the free particle, where the continuous parameter may label either position (e.g. x) or momentum (p) – but not both at the same time.

Morally, these all have the same basic underlying mathematical structure. However, in practice we need to distinguish between the first two cases and the latter two. The latter two involve an infinite-dimensional vector space and so the normal matrix intuition will break down a little bit.

2.2 Operators in Quantum Mechanics

Given the set of states, we can also define *operators* which are functions which map states to states. An operator $\mathcal{O}$ is a function

$$\mathcal{O} : |\psi\rangle \longrightarrow |\phi\rangle \tag{2.15}$$

In general, we might expect any form of operators. However, in quantum mechanics we shall only work with *linear operators.* Linear operators are ones which satisfy the linearity conditions, namely

$$\mathcal{O}\left(|\psi_1\rangle + |\psi_2\rangle\right) = \mathcal{O}\left(|\psi_1\rangle\right) + \mathcal{O}\left(|\psi_2\rangle\right) \tag{2.16}$$

and

$$\mathcal{O}\left(\lambda|\psi_1\rangle\right) = \lambda\mathcal{O}\left(|\psi_1\rangle\right) \tag{2.17}$$

Why does quantum mechanics only involve linear operators? This is a good question. Unfortunately, I don't have a good answer. The linearity of operators is one of the fundamental postulates of quantum mechanics and so one answer is just 'Because it is.' However, that does not feel fully satisfactory.

Let us give some examples of operators. Suppose we have a 3-dimensional quantum system, so we can construct an orthonormal basis of kets $\{|1\rangle, |2\rangle, |3\rangle\}$. Here are some examples of linear operators that act on this space of kets (and take kets to kets).

- The operator $|1\rangle\langle 3| + |3\rangle\rangle\langle 1|$.

  Note that an operator, in bra-ket language, is naturally written as ket-bra, so that it operates on a ket and returns a ket.

  In this case, for example,

$$\Big(|1\rangle\langle 3| + |3\rangle\langle 1|\Big)|3\rangle = |1\rangle. \tag{2.18}$$

- Another example is the *identity operator*, which I denote here by $\mathbb{I}$. This is defined by

$$\mathbb{I}|\psi\rangle = 1|\psi\rangle. \tag{2.19}$$

  Note the variety of roles the concept of 'identity' can play: both as an operator acting on kets, and also as the simple number 'one'.

Note that if the space of states is finite-dimensional, so we can construct a complete orthonormal basis $|\psi_i\rangle$, then these linear operators are more simply described as *matrices*. You probably first encountered matrices at school and, by now, they are part of your mental furniture. But recall the Max Born quote we saw earlier – 'Well known to mathematicians' indeed! How times have changed.

In many applications of quantum mechanics (for example, those involving particles and wavefunctions), the space of states is infinite-dimensional. Although matrices are not then the most efficient way to solve problems, you may find it useful to have them in the back of your mind as an intuition for the mathematical structure of the theory.

There is one further important restriction we want to put on the class of operators. This is to what are called *Hermitian operators*. Given an operator A, its Hermitian conjugate $A^\dagger$ is defined as the operator $A^\dagger$ such that

$$\langle\phi|A^\dagger|\psi\rangle = \left(\langle\psi|A|\phi\rangle\right)^* \tag{2.20}$$

A Hermitian operator is then one where $A^\dagger = A$, i.e. the operator is equal to its Hermitian conjugate. Another, perhaps more intuitive way of putting this, is that Hermitian operators are *real* operators. Hermitian operators corresponds to physical observables.

If the language of bras and kets originally comes across as slightly dry, it may be helpful to have a mental map in your mind linking to the language of complex vectors and their scalar products.

$$|\psi\rangle \longleftrightarrow \begin{pmatrix} \psi_1 \\ \psi_2 \\ \dots \\ \psi_n \end{pmatrix}$$

$$\langle\psi| \longleftrightarrow \begin{pmatrix} \psi_1^* \; \psi_2^* \; \dots \; \psi_n^* \end{pmatrix} \tag{2.21}$$

$$\langle\psi|\phi\rangle \longleftrightarrow \begin{pmatrix} \psi_1^* \; \psi_2^* \; \dots \; \psi_n^* \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \dots \\ \phi_n \end{pmatrix} = \sum_i \psi_i^* \phi_i \tag{2.22}$$

$$A \longleftrightarrow \begin{pmatrix} A_{11} & A_{12} & \dots & A_{1n} \\ A_{21} & A_{22} & \dots & \dots \\ \dots & & & \\ A_{n1} & A_{n2} & \dots & A_{nn} \end{pmatrix} \tag{2.23}$$

$$A^\dagger \equiv \left(A^T\right)^* \longleftrightarrow \begin{pmatrix} A_{11}^* & A_{21}^* & \dots & A_{n1}^* \\ A_{12}^* & A_{22}^* & \dots & \dots \\ \dots & & & \\ A_{1n}^* & A_{2n}^* & \dots & A_{nn}^* \end{pmatrix} \tag{2.24}$$

$$\langle\psi|A|\phi\rangle \longleftrightarrow \begin{pmatrix} \psi_1^* \; \psi_2^* \; \dots \; \psi_n^* \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} & \dots & A_{1n} \\ A_{21} & A_{22} & \dots & \dots \\ \dots & & & \\ A_{n1} & A_{n2} & \dots & A_{nn} \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \dots \\ \phi_n \end{pmatrix} \tag{2.25}$$

There are some key basic properties of Hermitian operators you should learn and not forget; you want to be able to use these properties without thinking about them.

1. Hermitian operators have real eigenvalues.

2. Eigenstates corresponding to different eigenvalues are orthogonal. If

$$A|\psi_i\rangle = \lambda_i|\psi_i\rangle \qquad \text{and} \qquad A|\psi_j\rangle = \lambda_j|\psi_j\rangle$$

with $\lambda_i \neq \lambda_j$, then it follows that

$$\langle \psi_i | \psi_j \rangle = 0. \tag{2.26}$$

3. We can use the eigenstates of a Hermitian operator to construct an orthonormal basis of the state space.

You probably saw proof of these results in the first-year Vectors and Matrices course; but let us recap them her in the language of bras and kets.

To see that eigenvalues are real (**first point**), we use the definition of a Hermitian operator from (2.20),

$$\langle \phi | A | \psi \rangle = \left(\langle \psi | A | \phi \rangle \right)^* \tag{2.27}$$

and put $|\phi\rangle = |\psi\rangle = |\psi_i\rangle$: that is, make both bras and kets an eigenket $|\psi_i\rangle$ of the operator $\hat{A}$, in an orthonormal basis. This gives

$$\langle \psi_i | A | \psi_i \rangle = \left(\langle \psi_i | A | \psi_i \rangle \right)^* \tag{2.28}$$

and so

$$\lambda_i = \lambda_i^*. \tag{2.29}$$

For the **second point** (that eigenstates corresponding to different eigenvalues are orthogonal), we take the separate eigenstates (denoted $|n\rangle$ and $|m\rangle$). Then

$$\langle n | A | m \rangle = \left(\langle m | A | n \rangle \right)^* \tag{2.30}$$

Using the reality of the eigenvalues, this becomes

$$\lambda_m \langle n | m \rangle = \lambda_n \left(\langle m | n \rangle \right)^* \tag{2.31}$$

where we can use the nature of the complex scalar product to write

$$\lambda_m \langle n | m \rangle = \lambda_n \langle n | m \rangle \tag{2.32}$$

and so

$$\left(\lambda_m - \lambda_n \right) \langle n | m \rangle = 0. \tag{2.33}$$

As $\lambda_m \neq \lambda_n$, it follows thar $\langle n | m \rangle = 0$.

For the procedure of obtaining an orthonormal basis **(third point)**, I simply refer you back to results from linear algebra / Vectors and Matrices.

2.3 Overall and Relative Phases

At the heart of quantum mechanics is the notion that (complex) amplitudes are more fundamental than probabilities. Complex amplitudes carry phases. When do these phases matter?

The basic idea is that *absolute* phases do not matter but *relative* phases do. To see this, suppose we have a basis of eigenstates $\{|1\rangle, |2\rangle, |3\rangle, \ldots |n\rangle\}$ and we re-phase them *all*, so

$$\{|1\rangle, |2\rangle, |3\rangle, \ldots |n\rangle\} \rightarrow e^{i\alpha}\{|1\rangle, |2\rangle, |3\rangle, \ldots |n\rangle\}. \tag{2.34}$$

Then any amplitude we construct by overlapping a state $|\psi\rangle$ with these kets changes by a common factor of $e^{i\alpha}$.

$$\langle\psi|i\rangle \rightarrow e^{i\alpha}\langle\psi|i\rangle. \tag{2.35}$$

In any computation of probabilities, this *common* phase will drop out – because it is common to everything.

Relative phases, on the other hand, matter greatly. For example, the states

$$|1\rangle + |2\rangle$$

and

$$|1\rangle + e^{i\alpha}|2\rangle$$

are completely different. We have introduced a relative phase between the two linear combination, and this entirely changes the ket.

The significance of relative phases can also be seen via the notion of interference:

$$|\mathcal{A}_1 + \mathcal{A}_2|^2 \neq |\mathcal{A}_1 + e^{i\alpha}\mathcal{A}_2|^2 \tag{2.36}$$

2.4 Hermitian Operators and Observables

The idea of an *observable* is key to the *physics* of quantum mechanics: observables are the empirical goods, as it were, that we can buy. When we do an experiment, an observable is the result that the experiment produces: it is something we can measure through data.

What results can we get? The basic rule is that the possible values you can get from a measurement are restricted to the eigenvalues of the relevant Hermitian operator. So, if you have a Hermitian operator $\mathcal{A}$ with eigenvalues λ_i, with $i = 1, \ldots n$, then the possible values you can get for the observable corresponding to $\mathcal{A}$ are the n possible values λ_i.

This is actually quite a strong statement. The reason for this is that it tells us that, when we measure a quantity, the only answers we can get are (in general) restricted to a very limited set of possible results: the eigenvalues of the corresponding operator. In some cases (one example that we will later see in more depth is that of angular momentum) the corresponding operator may only have a finite and discrete set of eigenvalues. For example, if we measure the intrinsic angular momentum of a spin-1/2 particle along a certain axis, we will *either* get the answer $+\hbar/2$ *or* the answer $-\hbar/2$: these are the only possible results.

There is one particular Hermitian operator present in all quantum mechanical systems. This is the *Hamiltonian* and is denoted by H. The Hamiltonian measures the energy of a system. A state $|\psi_n\rangle$ in an eigenstate of the Hamilton with eigenvalue E_n has energy E_n,

$$H|\psi_n\rangle = E_n|\psi_n\rangle \tag{2.37}$$

Such states (energy eigenstates of the Hamiltonian) play a special role in quantum mechanics. They may be called *energy eigenstates* or *stationary states* (depending on the context and literature).

Note that there is absolutely no requirement for the energy eigenvalues to be positive. In fact, we can always add a constant term to the Hamiltonian (or, more precisely, a constant times the identity operator) and this will shift all the energy eigenvalues by a constant amount.

Such a constant shift does not affect the physics, although there is a useful convention (especially applicable to bound systems like a Hydrogen atom) in which potential energies are taken to vanish at infinity: this is why we write the electrostatic potential as

$$U_{Coulomb} = \frac{Q_1 Q_2}{4\pi\epsilon_0 r} \tag{2.38}$$

and not

$$U_{Coulomb} = \frac{Q_1 Q_2}{4\pi\epsilon_0 r} + U_0 \tag{2.39}$$

What happens when a state is not an energy eigenstate and we try and measure the energy? Suppose we have a quantum-mechanical system, and we have a state expressed as a linear combination of two energy eigenstates,

$$|\psi\rangle = \alpha|E_1\rangle + \beta|E_2\rangle, \tag{2.40}$$

where $|\alpha|^2 + |\beta|^2 = 1$ to ensure the state $|\psi\rangle$ is normalised.

The only possible answer we can get from the measurement is one of the allowed energies, namely one of the energy eigenvalues. Either we measure E_1 or we measure E_2. The result is probabilistic, but set by the amplitudes for each state.

$$P(E_1) = |\alpha|^2 \tag{2.41}$$

$$P(E_2) = |\beta|^2. \tag{2.42}$$

This reflects a general property of observations in quantum mechanics. Even when the original state is perfectly known, the result of taking a measurement is only predictable probabilistically.

Generally, if we have a Hermitian operator A corresponding to an observable, then we can expand a general state in terms of eigenstates of A (for now, we assume that there are no degenerate eigenvalues). That is, an arbitrary state $|\phi\rangle$ can be written as

$$|\phi\rangle = \sum_i^n \alpha_i |a_i\rangle \tag{2.43}$$

For a normalised state, recall that $\sum |\alpha_i|^2 = 1$. When we prepare a quantum system in the state $|\phi\rangle$ and perform a measurement of observable A, the probability of measuring a_i and obtaining state $|a_i\rangle$ is $|\alpha_i|^2$. After the measurement, the state of the system is now $|a_i\rangle$.

Generally, if we decompose a general state $|\phi\rangle$ as a linear combination of eigenstates,

$$|\phi\rangle = \sum_i^n \alpha_i |a_i\rangle \tag{2.44}$$

then $\alpha_i = \langle\phi|a_i\rangle$ gives the amplitude for the state $|\phi\rangle$ to decompose into $|a_i\rangle$ under a measurement.

From this it is easy for us to work out an important concept, the *expectation value* of an observable. Physically, the expectation value is the (mean) average value of an observable if we would prepare a quantum state many times, and measure it many times. You may want to envision a gigantic undergraduate physics laboratory, with thousands of benches set up, on each of which a system has been prepared in the same well-defined quantum state. Every student at every bench measures the observable. As quantum mechanics is probabilistic not deterministic, they will get different values. What the expectation value tells us is the *mean average* of all these values, averaged over the number of students.

To be more specific, let us focus on the single most important observable, the energy, which corresponds to the *Hamiltonian operator* $\hat{H}$ (the term Hamiltonian picks up the corresponding quantity in classical mechanics). We suppose we have a state decomposed as a linear combination of energy eigenstates,

$$|\psi\rangle = \sum \alpha_n |E_n\rangle. \tag{2.45}$$

The expectation value of the energy is then the sum of the possible values of the measurement multiplied by the probability of obtaining each value,

$$\langle E\rangle = \sum_n \mathrm{Prob}(E_n) \times E_n \tag{2.46}$$

As the amplitude for the state $|E_n\rangle$ is α_n, this expectation value is given by

$$\langle E\rangle = \sum_n |\alpha_n|^2 \times E_n \tag{2.47}$$

Note this is equivalent to

$$\begin{aligned}
\langle E\rangle &= \langle\psi|\hat{H}|\psi\rangle && (2.48)\\
&= \sum_{n,m} \alpha_n^* \alpha_m \langle E_n|\hat{H}|E_m\rangle && (2.49)\\
&= \sum_{n,m} \alpha_n^* \alpha_m E_m \delta_{n,m} && (2.50)\\
&= \sum_n |\alpha_n|^2 E_n. && (2.51)
\end{aligned}$$

Indeed, as we go on we will use without further elaboration $\langle\psi|\hat{A}|\psi\rangle$ for the expectation value of the operator/observable $\hat{A}$ in the quantum state $|\psi\rangle$.

2.5 Measurement in Quantum Mechanics

Measurement in quantum mechanics is one of those topics that it is important to spend a certain amount of time thinking about, and then equally important to stop thinking about. Here we will describe what is the 'standard' account of measurement in quantum mechanics, called the *Copenhagen interpretation* (Copenhagen is where Niels Bohr was based, and so the Copenhagen interpretation dates to the earliest days of quantum mechanics). The topic of measurement shades into the various possible interpretations of quantum mechanics.

I am not going to be a strong advocate of any particular interpretation, or way of thinking about what ‘quantum reality’ represents. My own view is that too much time spent thinking about interpretative matters is dangerous for practising physicists (others will disagree). However, I do want to describe the Copenhagen interpretation, both for its historical importance and because it still represents the ‘default’ against which different interpretations are compared.

The first point concerns what can be measured. We can only measure quantities corresponding to Hermitian operators, or *observables* (as the name suggests). A measurement involves the use of some apparatus to determine the value of this observable.

Key to the notion of quantum measurement is the idea that, after the measurement, the system will be in an exact eigenstate of the Hermitian operator of the observable, *whether or not it was in such an eigenstate prior to the measurement.* In particular, if the *initial* state of the system was

$$|\psi\rangle = \sum_n \alpha_n |A_n\rangle, \tag{2.52}$$

where A_n correspond to the different eigenvalues of the Hermitian operator $\hat{A}$ and $\sum |\alpha_n|^2 = 1$, then when we do a measurement of A then afterwards the state of the system is

$$|\psi\rangle = |A_n\rangle \tag{2.53}$$

for whatever value A_n of the measurement we have obtained.

The probability of obtaining each value A_n is $|\alpha_n|^2$; the results of an individual measurement are strictly probabilistic and there is no way to say in advance what the result of an individual measurement will be. Although we can make probabilistic predictions that will hold for a large number of measurements, we can never definitively say what the outcome of a single measurement will be (note that this is very different from classical mechanics, where if we know the exact state of a system we can, in principle, say exactly what will happen if we measure it).

On hearing this last point, your first instinct might be to say: perhaps quantum mechanics is only an approximate theory, and there is extra stuff that we are missing. Perhaps the state vector is not everything, and there are additional hidden variables that we could also know about. If we knew these hidden variables, then the probabilistic nature of the measurement may cease to hold, and instead the result may be deterministic.

But nature is subtle, subtler by far than our primordial ape-brains trained by evolution to hunt prey and dodge predators. They sit too far outside the main part of this course for me to discuss them in detail, but there are a series of tests of hidden variable theories using what are called the *Bell inequalities* and associated with the *(Alain) Aspect experiments.* If you are interested, look them up. In every conflict so far between quantum mechanics and naive human intuition, quantum mechanics has won.

Note that, in the process of measurement, the state of the system (equivalently, the wavefunction) has changed from $|\psi\rangle = \sum_n \alpha_n |A_n\rangle$ to $|A_n\rangle$. This change is called the *collapse of the wavefunction* in the Copenhagen interpretation; in the Copenhagen interpretation we treat this as happening instantaneously at the moment of measurement.

The other main way of thinking about measurement in quantum mechanics is what is called the *Many Worlds Interpretation.* This argues that in the act of 'measurement', we have to recognise that the measuring apparatus is also a quantum system; the state of the 'system' is therefore entangled with the state of the measuring apparatus. The evolution of the full system through the process of measurement is what takes the initial state (which is a superposition of eigenstates of the operator $\hat{A}$) and effectively splits it into different branches of the wavefunction with unique and well-defined values of the eigenvalue.

With the Many Worlds Interpretation, the big question is why we only perceive ourselves as living on one branch of the wavefunction (this is the 'collapse' of the wavefunction.

The final standard interpretation of Quantum Mechanics, and probably the most popular among physicists, is the Suac Interpretation (*Shut Up and Calculate*).

But you are all free citizens of the scientific community: you get to choose your own preferred interpretation of quantum mechanics.

2.6 Commutation of Operators

The connection of operators to matrices should immediately alert to an aspect of quantum mechanics that was intensely strange when historically first encountered: the lack of commutation between operators. It should be familiar from your knowledge of matrices that the order of matrix multiplication matters:

$$AB \neq BA. \tag{2.54}$$

What holds for matrices also holds for operators. If we have two operators $\hat{A}$ and $\hat{B}$ acting on a ket, then (in general)

$$\hat{A}\hat{B}|\psi\rangle \neq \hat{B}\hat{A}|\psi\rangle. \tag{2.55}$$

It is best to think about operators in this way, as operators acting on kets. When one explicitly works out commutation relations, not including the ket is not *strictly* wrong, but in practice not thinking about the ket can be an easy way to make mistakes when determining the commutator.

(One example that may be obscure now but we will come to later: when thinking and the derivative operator $\hat{p} = -i\hbar\frac{\partial}{\partial x}$, if one forgets that this operator is acting on a wavefunction $\psi(x)$, then it is easy to make a mistake when commuting the derivative operator through another one).

Operators A and B are said to *commute* if

$$\hat{A}\hat{B}|\psi\rangle = \hat{B}\hat{A}|\psi\rangle \tag{2.56}$$

for *all* kets $|\psi\rangle$ (a common starting mistake is to think that this equation holding for a *particular* ket is the same as it holding for *all* kets). The *commutator* of two operators $\hat{A}$ and $\hat{B}$ is denoted by $\left[\hat{A}, \hat{B}\right]$ (note this is itself an operator):

$$\hat{A}\hat{B} - \hat{B}\hat{A}|\psi\rangle \equiv \left[\hat{A}, \hat{B}\right]|\psi\rangle \tag{2.57}$$

Note that the commutator is itself an operator, even if sometimes it is written as a number (for example, and anticipating a later point, you will often see written $[\hat{x}, \hat{p}] = i\hbar$, where $\hat{x}$ and $\hat{p}$ are the position and momentum operators). In fact, this is a good prompt for you to reflect on:

> What is the difference between *0 the number*, the *zero operator* and *nothing*?

Note that, although the commutator is constructed from Hermitian operators, the commutator is not itself a Hermitian operator. Indeed, it is reasonably easy to prove that if $\hat{A}$ and $\hat{B}$ are Hermitian operators the commutator $\left[\hat{A}, \hat{B}\right]$ is an *anti-Hermitian* operator (an operator $\hat{X}$ is anti-Hermitian if $\hat{X}^\dagger = -\hat{X}$).

Fluency in manipulating commutators is key to doing calculations in quantum mechanics. Some basic properties (which you should be able to prove):

1. $[A, A] = 0$
2. $[A, BC] = [A, B]\, C + B\, [A, C]$
3. $[A, BCD] = [A, B]\, CD + B\, [A, C]\, D + BC\, [A, D]$

The notion of commuting operators is important because it allows operators to be *simultaneously diagonalisable*, so that we can find a basis so that all kets are eigenkets of *both* $\hat{A}$ and $\hat{B}$, so that any ket $|\psi\rangle$ can be expressed as

$$|\psi\rangle = \sum \lambda_{ij} |a_i b_j\rangle \tag{2.58}$$

where

$$A|a_i b_j\rangle = a_i |a_i b_j\rangle \tag{2.59}$$

and

$$B|a_i b_j\rangle = b_j |a_i b_j\rangle \tag{2.60}$$

If we have found a basis in which the operators are simultaneously diagonalisable, it should be clear that

$$\begin{aligned} \left[\hat{A}, \hat{B}\right] |a_i, b_j\rangle &= \left(\hat{A}\hat{B} - \hat{B}\hat{A}\right) |a_i, b_j\rangle \\ &= \left(a_i b_j - b_j a_i\right) |a_i b_j) \\ &= 0. \end{aligned} \tag{2.61}$$

To go the other way, starting from a vanishing commutator $\left[\hat{A}, \hat{B}\right] = 0$: suppose that $\hat{A}$ and $\hat{B}$ commute. As they are both Hermitian operators, we can construct a basis of eigenstates of $\hat{A}$ such that a general state $|\psi\rangle$ can be expanded as a linear combination of eigenstates of $\hat{A}$,

$$|\psi\rangle = \sum_i \lambda_i |a_i\rangle \tag{2.62}$$

We know that

$$\left[\hat{A}, \hat{B}\right] |a_i\rangle = \left(\hat{A}\hat{B} - \hat{B}\hat{A}\right) |a_i\rangle = 0. \tag{2.63}$$

As $|a_i\rangle$ is an eigenstate of $\hat{A}$, we have

$$0 = \left(\hat{A}\hat{B} - \hat{B}\hat{A}\right) |a_i\rangle = \hat{A}\left(\hat{B}|a_i\rangle\right) - a_i \left(\hat{B}|a_i\rangle\right). \tag{2.64}$$

It follows that $\hat{B}|a_i\rangle$ is also an eigenstate of $\hat{A}$ with eigenvalue a_i. We can then diagonalise $\hat{B}$ restricted to the subset of states that are eigenkets of $\hat{A}$ with eigenvalue a_i, creating a complete basis of states that are simultaneous eigenkets of both $\hat{A}$ and $\hat{B}$.

Note that while A and B commuting means that $[A, B] \equiv 0$ as an operator equation, it doesn't mean that every ket has to be an eigenstate of A or B. It is important to note that the significance of *being able to find a basis where the operator is diagonal* is that we can express a generic ket as a linear combination of eigenkets, *not* that a generic ket is itself an eigenket.

In terms of physical significance, the importance of commuting operators is that the quantities they correspond to can be simultaneously measured. If A commutes with B, then physical quantity A can be known at the same time as physical quantity B: there is a basis of simultaneous eigenkets and we can always measure A and B at the same time. What it does *not* mean is that, if A and B commute, every eigenket of A is also an eigenket of B (this is explored in the problem sheets).

When two operators A and B do not commute, their commutator C is another operator,

$$[A, B] = C \tag{2.65}$$

In general, it is then not possible to measure A and B simultaneously. However, there can be circumstances where this statement is false, and we *can* measure A and B simultaneously despite their commutator being non-zero. What are these circumstances? This is explored in the problem sheets and I encourge you to think carefully about it.

Compatibility of observables

Suppose we measure two observables, $\hat{A}$ and $\hat{B}$. Let us suppose we first measure A and then measure B. Whatever the original ket, we will first of all obtain an eigenvalue of $\hat{A}$ (from the first measurement) and then an eigenvalue of $\hat{B}$ (from the second measurement): we will measure a_i and then b_j (with a certain probability, $P(b_j|a_i)$).

And we could do the same with B first instead of A: we could measure first of all observable B, and secondly observable A, to get b_j and then a_i (also with a certain probability $P(a_i|b_j)$).

Two observables are said to be *compatible* if these probabilities are the same: that is, in terms of ultimate experimental result it makes no difference about the order of measurement, and whether we measure A first and then B, or B first and then A.

Two observable are compatible when, and only when, their corresponding operators commute. You will show this on the problem sheets.

The Uncertainty Principle

We shall now prove the general form of the uncertainty principle. The uncertainty principle, often called *Heisenberg's Uncertainty Principle* is one of the most famous results of quantum mechanics, often described in popular accounts as being unable to know both the position and momentum of an object at the same time.

Slightly more precisely, this position-momentum uncertainty principle is written as

$$\Delta x \Delta p \geq \hbar/2, \tag{2.66}$$

where Δx and Δp are the uncertainties on the position and momentum of a particle.

Here we prove the general form of the uncertainty principle. We start with this for two reasons.

1. It makes it clear that the uncertainty principle arises as a general consequence of non-commuting operators.
2. As we have still not yet introduced the Schrödinger equation, it makes it clear that the uncertainty principle is a *kinematic* feature of quantum mechanics: it does not require *dynamics*, i.e. knowledge of the time evolution of the system.

Enough discussion. Let us suppose we have two Hermitian operators $\hat{A}$ and $\hat{B}$, and let $|\psi\rangle$ be a generic ket. We are going to start by considering the ket – or, more specifically, the norm of the ket

$$\left(\hat{A} + i\lambda\hat{B}\right)|\psi\rangle$$

where λ is a real number. Why do we do this? Good question! There is not an obvious reason why we should start with this particular ket, or be interested in its norm. We shall be justified by results, so I ask you here to trust that this is a sensible thing to do.

As the norm of the ket must be positive (or at least non-negative), we have the equation

$$\langle\psi|\left(\hat{A} - i\lambda\hat{B}\right)\left(\hat{A} + i\lambda\hat{B}\right)|\psi\rangle \geq 0. \tag{2.67}$$

Note that we have used here the fact that operators $\hat{A}$ and $\hat{B}$ are Hermitian and so $\hat{A}^\dagger = \hat{A}$. We can expand this out to give

$$\langle\psi|\hat{A}^2|\psi\rangle + i\lambda\langle\psi|\hat{A}\hat{B} - \hat{B}\hat{A}|\psi\rangle + \lambda^2\langle\psi|\hat{B}^2|\psi\rangle \geq 0, \tag{2.68}$$

that is

$$\langle\psi|\hat{A}^2|\psi\rangle + i\lambda\langle\psi|\left[\hat{A},\hat{B}\right]|\psi\rangle + \lambda^2\langle\psi|\hat{B}^2|\psi\rangle \geq 0. \tag{2.69}$$

We have not said very much about λ. We now want to extremise the LHS with respect to λ. Differentiating, the extremal value of λ occurs as

$$i\langle\psi|\left[\hat{A},\hat{B}\right]|\psi\rangle + 2\lambda\langle\psi|\hat{B}^2|\psi\rangle = 0 \tag{2.70}$$

and so

$$\lambda = -i\frac{\langle\psi|\left[\hat{A},\hat{B}\right]|\psi\rangle}{2\langle\psi|\hat{B}^2|\psi\rangle}. \tag{2.71}$$

We can substitute this value of λ back in to Eq. (2.69), to get

$$\langle\psi|\hat{A}^2|\psi\rangle + \frac{\langle\psi|\left[\hat{A},\hat{B}\right]|\psi\rangle^2}{2\langle\psi|\hat{B}^2|\psi\rangle} - \frac{\langle\psi|\left[\hat{A},\hat{B}\right]|\psi\rangle^2}{4\langle\psi|\hat{B}^2|\psi\rangle} \geq 0. \tag{2.72}$$

and so

$$\langle\psi|\hat{A}^2|\psi\rangle + \frac{\langle\psi|\left[\hat{A},\hat{B}\right]|\psi\rangle^2}{4\langle\psi|\hat{B}^2|\psi\rangle} \geq 0. \tag{2.73}$$

We can write this as

$$\langle\psi|\hat{A}^2|\psi\rangle\langle\psi|\hat{B}^2|\psi\rangle \geq \frac{\langle\psi|i\left[\hat{A},\hat{B}\right]|\psi\rangle^2}{4} \tag{2.74}$$

Now we are in business, as what we now have can be expressed as

$$\langle\hat{A}^2\rangle\langle\hat{B}^2\rangle \geq \frac{1}{4}\langle i\left[\hat{A},\hat{B}\right]\rangle^2. \tag{2.75}$$

This holds for any operators $\hat{A}$ and $\hat{B}$ on any ket $|\psi\rangle$. Given we can shift an operator by a constant (strictly, a constant multiple of the identity operator) and it does not affect the commutator, we can redefine the operators as $\hat{A} \to \hat{A} - \langle A\rangle_\psi$ and $\hat{B} \to \hat{B} - \langle B\rangle_\psi$ (the subscript ψ denotes the expectancy value in the state ψ), and we obtain

$$(\Delta A)^2\,(\Delta B)^2 \geq \frac{1}{4}\langle i\left[\hat{A},\hat{B}\right]\rangle^2, \tag{2.76}$$

which is indeed the general form of the uncertainty principle, applicable for all pairs of Hermitian operators $\hat{A}$ and $\hat{B}$.

In the case where $\hat{A} = \hat{x}$ the position operator and $\hat{B} = \hat{p}$ the momentum operator, then (as we will see later) $[\hat{x}, \hat{p}] = i\hbar$, and so we recover

$$(\Delta x)\,(\Delta p) \geq \frac{\hbar}{2}, \tag{2.77}$$

the standard form of the uncertainty principle – but note it holds for any pairs of operators, with the level of uncertainty set by their commutator!

3. Dynamics of Quantum Mechanics

So far we have discussed the mathematical framework of quantum mechanics. However, we have not put any *dynamics* in! If quantum mechanics is the theory of states, then we must be able to state how such states evolve with time. The question (which is almost a universal question in physics) is, if at time t_0 the state is $|\psi(t_0)\rangle$, what will the state be at any future time t_1?

3.1 Time-Dependent Schrödinger Equation

How do quantum states evolve in time? What is the fundamental evolution equation of quantum mechanics? Here we come to one of humanity's greatest achievements, the (time-dependent) Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle, \tag{3.1}$$

where H is the Hamiltonian operator for the system. Given a quantum mechanical system for which we know the Hamiltonian, this is how we can evolve a state forward over time.

We are not going to 'derive' the Schrödinger equation. No such thing is possible. The Schrödinger equation is a fundamental law of nature, and we do not know any more 'fundamental' basis or set of principles from which it is possible to derive these fundamental postulates of quantum mechanics.

Note: this does not include the 'collapse' of the wavefunction under measurements. One should view the evolving state as the 'pure' evolution without any measurement. Or, alternatively, regard the measurement as an interaction with an external device (that does the measurement) and which will drastically change the Hamiltonian for the period of the measurement. But, either way, regard the TDSE (Time-Dependent Schrödinger Equation) as the evolution for a pure system uncontaminated by any measuring device!

The TDSE is a very general equation; we have said very little about *which* quantum system we are dealing with or any of the details of what the *actual* Hamiltonian for a particular system is. However, it is very useful to look at some general properties. First, we examine how *eigenstates of the Hamiltonian* behave under the TDSE. That is, suppose we have a state $|\phi\rangle$ such that

$$\hat{H}|\phi\rangle = E|\phi\rangle, \tag{3.2}$$

i.e. $|\phi\rangle$ is an energy eigenstate of the Hamiltonian. How does $|\phi\rangle$ evolve as we move forward in time?

By direct substitution into the TDSE, we can verify that such an energy state $|\phi\rangle$ evolves as

$$|\phi(t)\rangle = e^{-iE(t-t_0)/\hbar}|\phi(t_0)\rangle, \tag{3.3}$$

where E is the corresponding energy eigenvalue. Energy eigenstates remain energy eigenstates, with a phase that simply rotates with a frequency depending on the energy: the higher the energy, the faster the rotation frequency.

This represents an important physics point: eigenstates of the Hamiltonian (energy eigenstates) *remain* eigenstates of the Hamiltonian as we evolve forward in time. This close connection between eigenstates of the Hamiltonian and a particularly simple behaviour under time evolution means that the energy eigenvalue equation is also called the Time-Independent Schrödinger Equation (TISE):

$$\hat{H}|\phi\rangle = E|\phi\rangle. \tag{3.4}$$

This equation, the TISE, simply identifies eigenstates of the Hamiltonian operator, namely the *energy eigenstates* or *stationary states.*

The TISE is crucial for understanding the structure of the physical system: the basis of energy eigenstates is the single most important basis of states. If we can find all solutions of the TISE, we know all the energy eigenstates. While the TISE does not directly give us the dynamical evolution of the system, if we know the energy eigenstates, and can decompose a generic state $|\psi\rangle$ as a linear combination of energy eigenstates, then – as we shall now see – we can read off the future evolution of the state from this decomposition.

To see this, let us consider a state which is not an eigenstate of the Hamiltonian but is instead initially a linear combination of two energy eigenstates.

$$|\phi(t=0)\rangle = \alpha|E_1\rangle + \beta|E_2\rangle \tag{3.5}$$

The evolution of $|\phi(t)\rangle$ with time is given by

$$|\phi(t)\rangle = \alpha e^{-iE_1t/\hbar}|E_1\rangle + \beta e^{-iE_2t/\hbar}|E_2\rangle \tag{3.6}$$

(please check this by substituting into the Schrödinger equation and confirming that it is satisfied!).

More generally, a sum over many energy eigenstates evolves with time as

$$|\phi(t)\rangle = \sum \alpha_n e^{-iE_n(t-t_0)/\hbar}|E_n\rangle, \tag{3.7}$$

which can also be checked by direct substitution into the Schrödinger equation.

Note that the time evolution described by Eq. (3.7) is entirely deterministic: given the initial configuration of the state at the initial time t_0, the subsequent evolution is completely and uniquely fixed for all time – apparently. How then do we reconcile this statement with the claim that quantum mechanics is intrinsically probabilistic?

It is the act of measurement that all the quantum woo or quantum weirdness occurs. It is in the act of measurement – whether through wavefunction collapse or through entanglement of the pure quantum state with that of the measurement apparatus – that precisely one eigenstate is (probabilistically) pulled out.

So, suppose we have the state of Eq. (3.7). In a measurement of energy, one – and only one of the eigenstates $|E_n\rangle$ – is picked out. We measure a definite energy E_n and the system collapses to the state $|E_n\rangle$ *in a probabilistic fashion* – the probability of collapse to the state $|E_n\rangle$ being set by the $P(E_n) = |\alpha_n|^2$. Before the measurement – and after the measurement – the evolution of the state is entirely deterministic and follows the Time-Dependent Schrödinger Equation. It is in the measurement that the *probabilistic and non-deterministic* act of collapse occurs.

Let us return to the general evolution

$$|\phi(t)\rangle = \sum \alpha_n e^{-iE_n(t-t_0)/\hbar} |E_n\rangle, \tag{3.8}$$

which is useful to illustrate a conceptual point about phases.

On one level, phases of quantum states are arbitrary: we can multiply any state by an arbitrary *overall* phase and it carries exactly the same physical information as it did previously. However, relative phases carry a lot of physics.

In particular, one subtle feature about the above evolution means that the *relative phase* between the two different energy eigenstates changes as a state evolves in time. Even if the *overall* phase does not matter so much, there is a huge difference between the states

$$e^{i\alpha}\left(|E_1\rangle + |E_2\rangle\right) \qquad \text{and} \qquad e^{i\alpha}\left(|E_1\rangle - |E_2\rangle\right) \tag{3.9}$$

as the *relative* phase between the two energy eigenstates $|E_1\rangle$ and $|E_2\rangle$ carries a lot of physics (one example, discussed in the lectures, is that of the physics of *neutrino oscillations*).

3.2 Ehrenfest's Theorem

We can use the Schrödinger equation to derive a general result for the evolution of expectation values. We want to consider

$$\frac{d}{dt}\langle\psi(t)|\hat{A}|\psi(t)\rangle = \left(\frac{d}{dt}\langle\psi(t)|\right)\hat{A}|\psi(t)\rangle + \langle\psi(t)|\hat{A}\left(\frac{d}{dt}|\psi(t)\rangle\right) \tag{3.10}$$

To get at this, realise that we have (from the TDSE)

$$\frac{d}{dt}|\psi(t)\rangle = \frac{-i}{\hbar}\hat{H}|\psi(t)\rangle \tag{3.11}$$

$$\frac{d}{dt}\langle\psi(t)| = \frac{i}{\hbar}\langle\psi(t)|\hat{H} \tag{3.12}$$

and so we can write

$$\frac{d}{dt}\langle\psi(t)|\hat{A}|\psi(t)\rangle = \frac{-i}{\hbar}\left(\langle\psi|\hat{A}\hat{H} - \hat{H}\hat{A}|\psi\rangle\right) \tag{3.13}$$

and so

$$\frac{d}{dt}\langle\psi(t)|\hat{A}|\psi(t)\rangle = \frac{-i}{\hbar}\langle\psi(t)|\left[\hat{A},\hat{H}\right]|\psi(t)\rangle, \tag{3.14}$$

which we can also condense into

$$\frac{d}{dt}\langle\hat{A}\rangle = \frac{-i}{\hbar}\langle\left[\hat{A},\hat{H}\right]\rangle. \tag{3.15}$$

This result is called *Ehrenfest's theorem.* It is one of the ways in which quantum mechanics maps back onto classical mechanics, as it involves the evolution of *expectation values*, which are simply classical numbers (as opposed to the evolutions of kets, which are intrinsically quantum objects).

3.3 Wavefunctions

The emphasis so far has been on the intuition of quantum mechanics as the structure associated to complex vectors, complex linear operators (matrices) and Hilbert spaces. That intuition is cleanest for finite-dimensional Hilbert spaces and also provides the right foundation to think about infinite-dimensional Hilbert spaces.

Which we shall now do! Here we think about the simplest (and important) case of an infinite-dimensional Hilbert space, that of a particle in a 1-dimensional space. In principle, the position of the particle can be at any point in the real axis, labelled as $x \in \mathbb{R}$. These position states form a complete basis of the Hilbert space, as $|x\rangle$. The state $|x\rangle$ corresponds to the particle being precisely at position x.

Normalisation of states now has some slight differences, to reflect the fact that the states are labelled by the continuous parameter x. In particular, the normalisation condition is

$$\langle x|y\rangle = \delta(x-y), \tag{3.16}$$

where $\delta(x-y)$ is the *Dirac delta function.* The Dirac delta function appears many times in quantum mechanics. It is a spike that is infinitely narrow and infinitely high, normalised such that the area under the spike is one. There are many ways to obtain the Dirac delta function as a limit of more conventional functions (for example, as a limit of a normalised Gaussian function where the width of the Gaussian is taken to zero while the area underneath is maintained at unity).

The key properties of the Dirac delta function $\delta(x-y)$ are

1. $\delta(x) = 0 \qquad \text{if} \qquad x \neq y.$
2. $\int_{y-\epsilon}^{y+\epsilon} \delta(x-y)dx = 1,$

where $\epsilon > 0$ is small. (These limits of the integral are chosen to ensure that the spike is precisely at $x = y$.)

What is the purpose of this normalisation? One reason is that there is no physically meaningful way in which an object can ever be *precisely* at any given point represented by an an infinitely thin strip along the number line. In practice, the best we can ever do is think about a highly localised particle, i.e. one with a ket

$$|\psi\rangle = \int \psi(x)|x\rangle dx \tag{3.17}$$

where the function $\psi(x)$ is sharply localised around some point x_0.

The expansion of Eq. (3.18),

$$|\psi\rangle = \int \psi(x)|x\rangle dx \tag{3.18}$$

reflects the fact that *any* state can be expanded as a linear combination of the basis states (here $|x\rangle$). Equivalently, this means that the function $\psi(x)$ provides a complete description of the ket $|\psi\rangle$ (or, at least, has all the information allowing us to write down the ket $|\psi\rangle$).

This function $\psi(x)$ is called the *wavefunction* for the particle, and is the quantity you probably encountered in any introductory popular account of quantum mechanics that you might have read.

Wavefunctions are localised states and so should be properly normalised. We want $\langle\psi|\psi\rangle = 1$ for a happily normalised state (note this a statement about the *ket* $|\psi\rangle$). What does the condition turn out to imply for $\psi(x)$?

$$
\begin{aligned}
\langle\psi|\psi\rangle &= \left(\int dy \langle y|\psi^*(y)\right) | \left(\int \psi(x)|x\rangle dx\right) \\
&= \int dx\, dy\, \psi^*(y)\psi(x)\langle y|x\rangle && (3.19) \\
&= \int dx\, dy\, \psi^*(y)\psi(x)\delta(x-y) && (3.20) \\
&= \int dx\, \psi^*(x)\psi(x) = \int dx |\psi(x)|^2. && (3.21)
\end{aligned}
$$

(Note that, very often, as done above we shall write the integrand to the right of dx). It follows from this that the normalisation condition of the wavefunction is

$$\int dx |\psi(x)|^2 = 1. \tag{3.22}$$

You should also verify, in a very similar fashion, that the overlap of two distinct kets $|\psi\rangle$ and $|\chi\rangle$ is

$$\langle\psi|\chi\rangle = \int dx\, \psi^*(x)\chi(x). \tag{3.23}$$

What, physically, does the wavefunction give us? Note that if we overlap the ket $|\psi\rangle$ with the bra $\langle x_0|$, we obtain

$$
\begin{aligned}
\langle x_0|\psi\rangle &= \int \psi(x)\langle x_0|x\rangle\, dx && (3.24) \\
&= \int \psi(x)\delta(x_0 - x) && (3.25) \\
&= \psi(x_0), && (3.26)
\end{aligned}
$$

and so the wavefunction $\psi(x)$ gives the *amplitude* to find a particle at x.

This amplitude is a *probability amplitude.* To convert it to a physical probability, of course we need to do a mod square of it, to get $|\psi(x)|^2$. However, there is another aspect associated to the fact that the variable x is a continuous one. In particular, the mod square $|\psi(x)|^2$ represents a probability density, $P(x)$, such that the probability to find a particle between x_0 and y_0 is

$$P(x_0 < x < y_0) = \int_{x_0}^{y_0} P(x) dx \equiv \int_{x_0}^{y_0} |\psi(x)|^2 dx \tag{3.27}$$

.

Note that there is an exact map between the ket $|\psi\rangle = \int dx \psi(x)|x\rangle$ and the wavefunction $\psi(x)$. It is therefore possible to write $\psi(x)$ as a way of describing the full quantum state of the system: for the moment, we will do this.

If $\psi(x)$ is the wavefunction, what are the operators that act on $\psi(x)$ (equivalent to operators acting on the ket)? The two most important operators are the *position operator* and the *momentum operator*, denoted as $\hat{x}$ and $\hat{p}$. The position operator acts as

$$\hat{x}\psi(x) = x\psi(x). \tag{3.28}$$

That is, the action of the position operator is to multiply the wavefunction by x. This is easy to see when thinking about the ket: it should be clear (using $\hat{x}|y\rangle = y|y\rangle$) that

$$\hat{x}\left(\int dy \psi(y)|y\rangle\right) = \int dy\, y\, \psi(y)\, |y\rangle \tag{3.29}$$

and so the resulting (un-normalised) wavefunction is $\psi_{new}(y) = y\psi_{old}(y)$. More generally, when acting on a wavefunction,

$$\hat{V}(x)\psi(x) = V(x)\psi(x). \tag{3.30}$$

The other important operator is the momentum operator, $\hat{p}$. This acts on a wavefunction as

$$\hat{p}\,\psi(x) = -i\hbar\frac{\partial}{\partial x}\psi(x,t). \tag{3.31}$$

The eigenfunctions of $\hat{p}$ are plane wave solutions,

$$\hat{p}Ae^{ikx} = \hbar k A e^{ikx} \tag{3.32}$$

What is the commutator of the position and momentum operator? This commutator is one of the great and important results in quantum mechanics and so let us work it out. What is $[\hat{x}, \hat{p}]$? We evaluate:

$$\begin{aligned}
[\hat{x},\hat{p}]\,\psi(x) &= (\hat{x}\hat{p} - \hat{p}\hat{x})\,\psi(x,t) && (3.33)\\
&= \left(x\left(-i\hbar\frac{\partial}{\partial x}\right) - \left(-i\hbar\frac{\partial}{\partial x}\right)x\right)\psi(x,t) && (3.34)\\
&= \left(-i\hbar x\frac{\partial\psi(x,t)}{\partial x} + i\hbar\psi(x,t) + i\hbar x\frac{\partial\psi(x,t)}{\partial x}\right) && (3.35)\\
&= i\hbar\psi(x,t). && (3.36)
\end{aligned}$$

This calculation appears straightforward, but has a banana skin in it. The banana skin is to ensure that when doing the calculation you remember that $\hat{x}$ and $\hat{p}$ are operators and so must act on the wavefunction $\psi(x,t)$ on the right hand side. This is important for the derivative operator: it has stuff to act on!

From the above calculation we infer that

$$[\hat{x}, \hat{p}] = i\hbar. \tag{3.37}$$

Well, perhaps. Remember that the commutator of operators is always another *operator*. It is easy to misunderstand the right hand side of the preceding equation, and so we make the right hand side completely explicit.

$$[\hat{x}, \hat{p}] = i\hbar\,\mathbb{I} \tag{3.38}$$

where $\mathbb{I}$ is the identity operator. This makes it clear that the right-hand side is an *operator*, not a *number*. This may sound like pedantry, but one danger of the wavefunction approach is that we obscure the difference between operators and regular numbers.

The non-commutation of the position and momentum operators in quantum mechanics is at the heart of the Heisenberg uncertainty principle, which saw earlier and now restate:

$$(\Delta x)\,(\Delta p) \geq \frac{\hbar}{2}. \tag{3.39}$$

The uncertainty principle (a) tells us that we can *never* know both the position and momentum of a single particle (b) quantifies this uncertainty, by telling us exactly what the limits are on our knowledge (this is what the numerical factor on the right hand side of the equation gives us).

Classical Harbingers of the Uncertainty Principle (Non-Examinable)

The better we know the position, the worse we know the momentum. Is this concept novel to quantum mechanics, or have we (or our illustrious ancestors on physics) seen it before? Are there other parts in physics from which we can draw on our stock of intuition to get an insight into this famous result?

Actually, yes – in at least two areas. The first comes from the classical physics of waves (and, in terms of the wavefunction formalism and wave/particle duality, can be viewed as mathematically equivalent to what goes on in the uncertainty principle). While an idealised wave consists only of a single frequency, wavepackets involve a sum over frequencies. The more localised the wavepacket, the greater the range of frequencies we need to include. No singer can ever make a perfect note at a single frequency – any signal localised in time must always contain a range of frequencies, and the more localised in time the signal is, the greater the range of frequencies.

A similar behaviour is also familiar in everyone's favourite undergraduate subject of optics, when we consider the image produced by light passing through a diffraction grating. The image produced on the resulting screen is set by the Fourier transform of the diffraction grating: and so the smaller the width L of the grating, the larger the spread X of the resulting signal: roughly $X \sim L^{-1}$.

However, the closest conceptual link to the uncertainty principle comes from a slightly more advanced area which you might not have seen (it will be discussed in S7 Classical Mechanics). This is *Liouville's theorem* in classical mechanics. This states that in Hamiltonian mechanics, the volume in phase space is conserved. Phase space is the parametrisation of the allowed space of a classical system by position and momentum variables. Evolution of a classical system involves a trajectory in this space, $(\mathbf{x}(t), \mathbf{p}(t))$.

Liouville's theorem is the statement that volume (or area, for the simplest systems with only one pair of position/momentum coordinates) in phase space is conserved. Liouville's theorem states that if we construct a surface $\delta\Sigma$ in phase space bounding a volume Σ, then the volume contained within that surface will be conserved during the evolution of the classical system:

$$\mathbf{Vol} = \int_{\Sigma} d\mathbf{x} d\mathbf{p} \tag{3.40}$$

is conserved over the evolution of the system within phase space.

Why is this a classical harbinger of the quantum uncertainty principle? Because it involves a trade-off between position and momentum. Consider the simplest case of a 1-dimensional system with a single position/momentum pair. If this system starts off localised in position-space, but de-localised in momentum space, then as the phase space volume is conserved, any gain in momentum localisation has to be paid for by a similar de-localisation in position space.

We should not stretch analogies too far – classical physics has no notion of quantisation (there is no $\hbar$) and Liouville's theorem applies only to the overall volume in phase space (for multi-dimensional systems) and not to individual pairs of position/momentum operators. Nonetheless, it is useful as a way of realising that the uncertainity principle is strange – but not emphquite as strange as it might first seem.

4. Single-Particle Hamiltonians

We now want to explore the quantum mechanics of various simple single-particle quantum systems – this is what all this work on building up formalism is leading up to! We start with the simplest example of a 1-dimensional system, the particle in an infinite square well.

What?

Why is the particle in an infinite square well the simplest quantum system? Why not the free particle?

The infinite square well is indeed the simplest system, as with a free particle there are lots of subtleties about normalising the wavefunction. Contain your (our) impatience, and we will come back to that next.

4.1 Particle In a Infinite Square Well

So let us examine the simplest quantum-mechanical system: a particle in a infinitely deep box, bounded at $x = 0$ and $x = L$. Picking up from classical mechanics, the form of the Hamiltonian is[2]

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x}), \tag{4.1}$$

where m is the mass of the particle. In this case the potential $V(\hat{x})$ is

$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \le x \le L \\ \infty & x > L \end{cases} \tag{4.2}$$

Good quantum mechanics know that we first obtain the energy eigenstates so that we can expand a general state as a linear combination of energy eigenstates: so we set up the Time-Independent Schrödinger Equation to do this. The equation we need to solve is

$$\left(-i\hbar\frac{\partial}{\partial x}\right)^2 \psi(x) = E\psi(x), \tag{4.3}$$

to obtain the eigenstates and eigenvalues. What is the significance of an infinitely deep box? There are two ways to think about this.

---

[2] although strictly this is an *assumption*, we can generally do the quantum mechanics of particles by taking classical Hamiltonians and promoting the coordinates to operators.

The first, slightly less smooth, way is to say that an infinitely deep box means that the particle can never be found outside the box (this is true as it would cost an infinite amount of potential energy). As a consequence, we must set the wavefunction to zero outside the box. That is, we impose boundary conditions

$$\psi(x) = 0 \qquad \text{for} \qquad x \leq 0 \text{ and } x \geq L \tag{4.4}$$

The above argument is not wrong, but it is a little artificial and done-by-hand. A better approach is to think about the particle 'in an infinite well' as the particle in the potential of Eq. (4.2), with a Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} \tag{4.5}$$

$$= \frac{\hat{p}^2}{2m} + \hat{V}(x). \tag{4.6}$$

What then happens when we try to solve the TISE,

$$\left(\frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial x} \right)^2 + V(x) \right) \psi(x) = E\psi(x)? \tag{4.7}$$

The fact that $V(x)$ is infinite outside the well renders it impossible to solve the TISE unless $\psi(x) = 0$ outside the well. In this way, we are returned to the idea of boundary conditions of

$$\psi(x) = 0 \qquad \text{for} \qquad x \leq 0 \text{ and } x \geq L \tag{4.8}$$

Our eigenvalue equation is then

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_n}{\partial x^2} \psi(x) = E_n \psi_n(x) \tag{4.9}$$

subject to the boundary conditions. It is easy to see that the appropriate solutions are sinusoidal functions, with

$$\psi_n(x) = A_n \sin\left(\frac{n\pi x}{L} \right) \tag{4.10}$$

with normalisation $A_n = \sqrt{\frac{2}{L}}$ and eigenvalues

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}. \tag{4.11}$$

We have solved the system! We now have wavefunctions and energy eigenstates, and can expand generic states in terms of these.

4.2 The Free Particle

We next look at the surprisingly subtle case of the free particle. It might seem odd to look first at the case of a particle in a box, and then afterwards to look at the free particle. However, the system of a free quantum-mechanical particle contains various subtleties that are absent from the case of a particle in a box.

Let us set the system up. With an entirely free particle, the potential is $V(x) = 0$ for all values of x and so the Schrödinger equation for a wavefunction $\psi(x)$ is then

$$\frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2 \psi(x) = E\psi(x), \tag{4.12}$$

i.e.

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\psi(x). \tag{4.13}$$

It is not difficult to find solutions of Eq. (4.13); the eigenfunctions are

$$\psi(x) = Ae^{\pm ikx}, \tag{4.14}$$

with corresponding energy eigenvalues $\frac{\hbar^2 k^2}{2m}$ and momentum eigenvalues $\pm\hbar k$.

If we also extend to the TDSE, it is easy to see that these solutions extend to time-dependent wavefunctions,

$$\psi(x) = Ae^{\left(\pm ikx - i\frac{E}{\hbar}t\right)}, \tag{4.15}$$

namely

$$\psi(x) = Ae^{\left(\pm ikx - i\frac{\hbar k^2}{2m}t\right)}, \tag{4.16}$$

Note that we can combine the $\pm k$ modes to create a different basis of energy eigenstates (which are now *no longer* also momentum eigenstates),

$$\psi(x) = A\sin(kx) \qquad \text{and} \qquad \psi(x) = B\cos(kx). \tag{4.17}$$

This latter basis represents standing waves; they are not momentum eigenstates as they are superpositions of right-moving ($+k$) and left-moving ($-k$) eigenstates – recall that standing waves arise as the superposition of right-moving and left-moving waves. Also note that if we plot these standing wave solutions, in many ways they look very similar to the wavefunctions for a particle in an infinite box.

But – and this is a big but – the normalisation is much more subtle. How do we normalise these wavefunctions? If we try and solve

$$\int dx\, \psi^*(x)\psi(x) = 1, \tag{4.18}$$

we find that it is impossible: this normalisation condition reduces to

$$\int_{-\infty}^{+\infty} dx\, \frac{1}{2}|A|^2 = 1 \tag{4.19}$$

which either cannot be solved or results in the absurd normalisation $A = \sqrt{2/\infty}$.

What has gone wrong here? And, correspondingly, how do we deal with free particles in quantum mechanics? This is a subtle question, and there are two ways to answer it.

In understanding the answer, it is helpful to think more carefully about the problems with the wavefunctions we have found, such a Ae^{ikx}. Such a wavefunction does not, in fact, look like any free particle we have ever seen. When we think of particles, we almost certainly think of something we can see (or at least detect) interacting with matter as it passes through it. Recall the most elementary particle detector is the Mark I eyeball, in which photons interact with rods and cones at the back of the eye.

On our normal understanding, a particle is – at least roughly –*somewhere*. However, the wavefunction Ae^{ikx} is an *anywhere*. It is entirely delocalised: it stretches throughout all of space and extends to the further reaches of infinity. Indeed, given this is a momentum eigenstate, this *must* be the case as a consequence of the uncertainty principle: perfect localisation in momentum space (and Ae^{ikx} is certainly a momentum eigenstate) is equivalent to infinite delocalisation in position space. Indeed, what we have in Ae^{ikx} is a something like a perfect wave: one with no structure that can correspond to the lumpiness of an actual particle.

There are two ways we can now understand what has gone 'wrong'. The first starts by making an analogy to sound waves and recalling that interesting sound transmissions are never single frequencies, but instead consist of wavepackets: a superposition of close but not-quite-identical frequencies which generate a wavepacket that can be localised in position and can transmit structure and information from A to B.

In exactly the same way, we can also construct a *wavepacket*, an ensemble localised around a certain frequency k_0 (the 'classical' frequency),

$$\psi_{particle}(x) = \int_{k_0-\epsilon}^{k_0+\epsilon} f(k) e^{ikx} dk. \tag{4.20}$$

As $p = \hbar k$, the central frequency sets the classical speed of the wavepacket as $v = \hbar k_0/m$.

Such an ensemble of waves – a wavepacket – can certainly be localised in position space, with $\Delta x \Delta p \sim \hbar$ and so $\Delta x \Delta k \sim 1$. Consequently, there is no problem with normalising such a wavefunction to satisfy

$$\int dx\, \psi^*(x)\psi(x) = 1. \tag{4.21}$$

Note that the wavefunction $\psi_{particle}(x)$ is not an exact eigenstate of the momentum and so is not an exact eigenstate of the Hamiltonian (how can it be, when it is explicitly constructed as a superposition of different momentum eigenstates?). However, for practical (and classical) purposes we can certainly think of it as having a well-defined momentum. If we can only measure momentum with a certain resolution, then for practical purposes all the different momentum eigenstates have the 'same' momentum: and so we can make contact with the description of classical mechanics where particles have a single and well-defined momentum – yes, strictly these are wavepackets involving a superposition of momentum eigenstates, but ordinary equipment lacks the sensitivity to resolve any difference in these momentum eigenvalues.

The time-dependent version of the wavepacket is

$$\psi(x,t) = \int_{k_0-\epsilon}^{k_0+\epsilon} dk A(k) e^{\left(ikx - i\frac{\hbar k^2}{2m}t\right)}, \tag{4.22}$$

From this we can also see that the group velocity of the wavepacket is $v_g = \frac{\partial \omega}{\partial k} = \frac{\hbar k}{m}$ which is indeed the classical speed of a particle, p/m, as indeed it ought to be.

Strictly, if we want to study scattering of single particles in quantum mechanics then we should work with wavepackets. These are properly normalised and are honest-to-good descriptions of single particles. However, this formalism is cumbersome. The wavepackets are neither momentum nor energy eigenstates, and their evolution is strongly time-dependent (as the packet moves forward in time before scattering off the barrier).

We really don't want to work like this unless we have to!

However, it is fortunate that for all practical calculational purposes we can adopt a simpler approach which – it can be shown – reproduces the results from the more precise wavepacket approach above. On this approach, we do just use the un-normalised wavefunction

$$\psi(x) = Ae^{ikx} \tag{4.23}$$

to describe a free particle. Can we give a sensible interpretation of this? Yes, we can. We should think of the wavefunction Ae^{ikx} not as a single particle, but as a plane wave wavefunction describing a continuous stream (or beam) of particles from left to right with momentum $\hbar k$.

In doing this, we give up on treating this as a normalised single-particle wavefunction, which would require $\int dx\, \psi^* \psi = 1$, and instead treat the wavefunction as representing a particle density, so that $\int_a^b dx\, \psi^* \psi = N$, where N is the (expected) total number of particles between a and b, with $|\psi|^2$ giving the number density of particles.

It is true but not obvious – and the proof is beyond the scope of this course – that calculations of single particle scattering, reflection, transmission etc can all be successfully done using these wave solutions, involving simple wavefunctions of the form Ae^{ikx}, rather than requiring us to use wavepacket with their complicated time-dependent evolution. A great advantage of the former (involving Ae^{ikx} and the like) is that we can use the time-*independent* energy eigenstates for the calculation, representing a continual steady state beam of particles. In contrast, for single-particle wavepackets, we would need to use an explicitly time-dependent formalism to track the evolution of the wavepacket in time.

So, following this conceptual explanation, we can finally return to our free-particle wavefunction solving the free Time-Independent Schrödinger Equation (seen above as Eqs. (4.21) and (4.22)),

$$\frac{-\hbar^2}{2m}\frac{\partial^2 \psi(x)}{\partial x^2} = E\psi(x), \tag{4.24}$$

with

$$\psi(x) = Ae^{ikx} \tag{4.25}$$

and

$$E = \frac{\hbar^2 k^2}{2m}. \tag{4.26}$$

These can easily be extended to solutions of the TDSE,

$$\frac{-\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} = -i\hbar\frac{\partial \psi(x,t)}{\partial t}, \tag{4.27}$$

with the resulting free-particle wave solution being

$$\psi(x,t) = Ae^{i(kx-\omega t)}, \tag{4.28}$$

with $\omega = E/\hbar = \frac{\hbar k^2}{2m}$. These modes are both *energy* and *momentum* eigenstates. Through superposition of momentum eigenstates with $\pm k$ we can construct an energy eigenstate that is not a momentum eigenstate (for equal amplitude of the $+k$ and $-k$ modes, this corresponds to a standing wave).

4.3 Probability Density Current

Having introduced the notion of particle waves and wavepackets, now is a good time to introduce the notion of a probability density current, a vector that measures the flow of probability through space. For quantities like wavepackets, it is clear that probability flows from A to B. What the probability density current does is make this quantitative: it puts equations behind the words.

Currents and vectors are more intuitive in three dimensions. For this reason, we first define the 3-dimensional Schrödinger equation for a particle,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)\right)\psi(x,y,z,t) = i\hbar\frac{\partial\psi(x,y,z,t)}{\partial t}, \tag{4.29}$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. Clearly, this has wave solutions of the form

$$\psi(\mathbf{x},t) = Ae^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)}, \tag{4.30}$$

(where we use bold font for vectors $\mathbf{x} = (x,y,z)$) which describe propagation in the direction of the wavevector $\mathbf{k}$. For more general wavepacket solutions, what is the quantity that describes the flow of probability?

The answer – the probability density current – is the quantity

$$J(\mathbf{x},t) = \frac{i\hbar}{2m}\Big[\psi(\mathbf{x},t)\underline{\nabla}\psi^*(\mathbf{x},t) - \psi^*(\mathbf{x},t)\underline{\nabla}\psi(\mathbf{x},t)\Big]. \tag{4.31}$$

We have underlined the ∇ to make it clear that this is a vector. This vector describes the flow of probability current. How do we see this?

The continuity equation that must be satisfied by such a probability density current is

$$\underline{\nabla}\cdot J(\mathbf{x},t) = -\frac{\partial\rho(\mathbf{x},t)}{\partial t}. \tag{4.32}$$

To see this, note that if we integrate and use the divergence theorem, we have

$$\iiint \underline{\nabla}\cdot J(\mathbf{x},t)\,dV = \iint J(\mathbf{x},t)\cdot d\Sigma = -\iiint \frac{\partial\rho(\mathbf{x},t)}{\partial t}dV, \tag{4.33}$$

which represents the statement that the outflow of probability from a surface equals the change in probability from the voluem inside that surface.

What happens when we evaluate $\underline{\nabla} \cdot J(\mathbf{x}, t)$? We obtain

$$\begin{aligned}
\underline{\nabla} \cdot J(\mathbf{x}, t) &= \frac{i\hbar}{2m}\Big[\psi(\mathbf{x}, t)\,\underline{\nabla}^2\psi^*(\mathbf{x}, t) - \psi^*(\mathbf{x}, t)\,\underline{\nabla}^2\psi(\mathbf{x}, t)\Big] \\
&= -\psi(\mathbf{x}, t)\frac{\partial \psi^*(\mathbf{x}, t)}{\partial t} - \psi^*(\mathbf{x}, t)\frac{\partial \psi(\mathbf{x}, t)}{\partial t} && (4.34) \\
&= -\frac{\partial}{\partial t}(\psi^*(\mathbf{x}, t)\psi(\mathbf{x}, t)) && (4.35) \\
&= -\frac{\partial \rho(\mathbf{x}, t)}{\partial t}, && (4.36)
\end{aligned}$$

as required. The vector J therefore correctly describes the flux of probability and so represents a probability current density in quantum mechanics.

4.4 Scattering Problems: Matching Conditions for Wavefunctions

We now want to consider scattering problems where a wave is incident from $x = -\infty$ towards $x = +\infty$. Inbetween, it encounters features in the potential. The general style of the problem is to determine the amplitude for reflected and transmitted waves.

Note: why is this called a *scattering* problem? To understand this, we need to think about moving from a 1d problem to a 3d problem. In a 3d problem, when a beam of particle is fired in to a central potential, then scattered particles can be deflected at arbitrary angles (θ, ϕ) from the initial beam (you will study this more in B4 Particle Physics next year) – a very clear and proper scattering problem.

If we restrict to one spatial dimension, then 'scattering' has only two options: zero degrees (the transmitted wave) and one hundred and eighty degrees (the reflected wave). This is the reason why I shall refer to problems with incident, reflected and transmitted waves as 'scattering' problems: they are the baby, one-dimensional version of authentic 3d scattering problems involving particles incident on a central potential (such as that provided by an atomic nucleus).

In 1d scattering problems, an important role is played by the matching conditions for wavefunctions. These conditions concern (a) continuity of the wavefunction and (b) continuity of the first derivative of the wavefunction.

In terms of condition (a), this is an absolute requirement: the wavefunction must be continuous everywhere,

$$\psi(x_0)^- = \psi(x_0)^+, \tag{4.37}$$

i.e. the wavefunction is continuous at any join and takes the same value whether we approach from above or below. The physical reasons for this can be understood by thinking about the form of the momentum operator $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$. This is sensitive to the *derivative* of the wavefunction: any discontinuous wavefunction has an infinitely sharp derivative at that point, which corresponds to the presence of infinitely high momentum modes – which require infinitely high kinetic energy. As such, the wavefunction must be continuous to ensure it represents a physical (finite-energy) state.

The continuity condition for the first derivative of the potential is more subtle. It is true that, for any *finite* jump in potential, the first derivatives of the wavefunction remains continuous, with

$$\frac{\partial\psi}{\partial x}(x_0)^- = \frac{\partial\psi}{\partial x}(x_0)^+, \tag{4.38}$$

and taking the same value whether we approach it from above or below. However, this does not hold for infinite jumps in potential or cases involving a delta function.

To derive the appropriate matching condition, it is easiest to start with the Schrödinger equation for an energy eigenstate,

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x), \tag{4.39}$$

and study this equation in the vicinity of x_0.

In particular, we integrate Eq. (4.39) from $x_0 - \epsilon$ to $x_0 + \epsilon$ (where ϵ is very small). This gives

$$\int_{x_0-\epsilon}^{x_0+\epsilon} \frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x)\,dx = \int_{x_0-\epsilon}^{x_0+\epsilon} E\psi(x)\,dx. \tag{4.40}$$

For finite energy wavefunctions, E is finite. $\psi(x)$ is also finite. This means we can simplify Eq. (4.40) to

$$\frac{-\hbar^2}{2m}\left[\frac{\partial\psi(x)}{\partial x}\right]_{x_0-\epsilon}^{x_0+\epsilon} + \int_{x_0-\epsilon}^{x_0+\epsilon} V(x)\psi(x)\,dx = \mathcal{O}\left(\epsilon\right). \tag{4.41}$$

($\mathcal{O}(\epsilon)$ denotes a term of size ϵ in the limit that we take $\epsilon \to 0$). If $V(x)$ is finite and continuous, then it follows that we have

$$\frac{-\hbar^2}{2m}\left[\frac{\partial\psi(x)}{\partial x}\right]_{x_0-\epsilon}^{x_0+\epsilon} + \mathcal{O}\left(\epsilon\right) = \mathcal{O}\left(\epsilon\right) \tag{4.42}$$

and so as we take the limit $\epsilon \to 0$, then to ensure that the left-most term will also vanish as $\epsilon \to 0$ we recover the promised continuity condition of Eq. (4.43),

$$\frac{\partial\psi}{\partial x}(x_0)^- = \frac{\partial\psi}{\partial x}(x_0)^+. \tag{4.43}$$

However, if $V(x) = V_0\delta(x - x_0)$, then we now have

$$\frac{-\hbar^2}{2m}\left[\frac{\partial\psi(x)}{\partial x}\right]_{x_0-\epsilon}^{x_0+\epsilon} + \int_{x_0-\epsilon}^{x_0+\epsilon} V(x_0)\delta(x - x_0)\psi(x)\,dx = \mathcal{O}\left(\epsilon\right), \tag{4.44}$$

which becomes

$$\frac{-\hbar^2}{2m}\left(\frac{\partial\psi}{\partial x}(x_0)^+ - \frac{\partial\psi}{\partial x}(x_0)^+\right) + V(x_0)\psi(x_0) = \mathcal{O}\left(\epsilon\right). \tag{4.45}$$

In this case there are two finite terms remaining as we take the limit $\epsilon \to 0$, and so for consistency we require the jump condition

$$\frac{\partial\psi}{\partial x}(x_0)^+ - \frac{\partial\psi}{\partial x}(x_0)^+ = \frac{2m}{\hbar^2}V(x_0)\psi(x_0). \tag{4.46}$$

4.5 Particle Incident on a Step Potential

The simplest scattering problem is of a particle incident on a step potential described by

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x \geq 0 \end{cases} \tag{4.47}$$

We assume the particle (or beam of particles) is incident from the $x = -\infty$ limit and travels from left to right.

For $x < 0$ the Schrödinger equation is just that of the free particle. For $x > 0$ the Schrödinger equation is that of a free particle with an offset of V_0 in the potential. For an energy eigenstate of energy E, the Time-Independent Schrödinger Equation is then

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = E\psi(x), \qquad x < 0 \tag{4.48}$$

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = (E - V_0)\psi(x), \qquad x \geq 0 \tag{4.49}$$

The free particle Schrödinger equation for fixed energy exhibits two solutions: waves in the $+x$ and $-x$ direction, Ae^{ikx} and Be^{-ikx}.

Given that the physics of the problem involves waves incident from $x = -\infty$, we expect to have an incident wave, a reflected wave and a transmitted wave. We can therefore write the wavefunction as

$$\psi(x) = \begin{cases} Ie^{ikx} + Re^{-ikx} & x < 0 \\ Te^{ik'x} & x \geq 0 \end{cases} \tag{4.50}$$

where we use I, R and T to denote the amplitudes of incident, reflected and transmitted waves. Note that the amplitude of I is arbitrary (it specifies how intense the incoming wave is). The wavevectors k and k' are given by

$$k = \sqrt{\frac{2mE}{\hbar^2}} \tag{4.51}$$

$$k' = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} \tag{4.52}$$

Note that if $E < V_0$ then the wavevector k' is imaginary. This corresponds to the case of a classically forbidden step, with the energy of the incident particle less than the step potential. In quantum mechanics, the imaginary k' implies that the wavefunction is exponentially decaying (evanescent) in the classically forbidden area. We can heuristically view this as the quantum particle being able to penetrate a small distance into the classically forbidden region before it bounces back.

In the case of $E > V_0$ then the particle can pass into the $x > 0$ region, but as with any wave problem we expect there also to be reflection from the step.

To solve the problem we simply impose matching conditions at the boundary, namely continuity of ψ and $\frac{\partial \psi}{\partial x}$ at $x = 0$. These matching conditions produce the equations

$$I + R = T \tag{4.53}$$

and

$$k(I - R) = k'T. \tag{4.54}$$

Eliminating T, we have $(1 - k/k')\, I + (1 + k/k')\, R = 0$ and so

$$R = \left(\frac{\frac{k}{k'} - 1}{\frac{k}{k'} + 1} \right) I. \tag{4.55}$$

For the case that k' is imaginary (where the particle lacks energy to cross the step), it should be straightforward to see that $\left| \frac{\frac{k}{k'} - 1}{\frac{k}{k'} + 1} \right| = 1$ and so $|R|^2 = |I|^2$ (indeed, this is what we should expect as no particles can be transmitted to the $x = +\infty$ regime and so there is one hundred percent reflection).

4.6 The Finite Potential Well

We now consider the single-particle Hamiltonian for the case of a finite potential well. This is described by a potential,

$$V(x) = \begin{cases} 0 & |x| > a \\ -V_0 & |x| \leq a \end{cases} \tag{4.56}$$

In the limit $V_0 \to \infty$, the well turns into an infinite potential well.

We first address a conceptual aspect of this problem (this is the first of many times this particular conceptual aspect will be encountered in quantum mechanics, although it may be familiar from classical mechanics) where it is important to gain an intuition for how such problems work.

For this purpose, the particular feature I want to focus on is that there are two classes of solution to the energy eigenstate problem ($\hat{H}\psi_n(x) = E_n\psi_n(x)$), written out as

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi_n(x) = E_n\psi_n(x) \tag{4.57}$$

These two classes of solution are distinguished by whether $E_n > 0$ or $E_n < 0$, namely whether the energy eigenvalue is positive or negative. The former class of solutions corresponds to *unbound* solutions and the latter class of solutions corresponds to *bound* solutions. The significance of this difference is that it determines whether or not a particle can 'escape to infinity'. Unbound solutions can escape to infinity, whereas bound solutions cannot.

This concept ought to be familiar from (for example) gravitational systems. In orbital motion around a central massive source, objects can be in either bound orbits (in the way the earth is bound to the sun) or in unbound orbits (such as high-velocity objects passing through the solar system). As the potential energy at infinity is zero, the positive energy solutions have sufficient energy to reach infinity whereas the negative energy ones cannot (and, thus, these represent a bound solution).

So, we expect two types of solution: one with $E < 0$ which represent particles bound inside the box and also solutions with $E > 0$ that look like free particles. The latter type of solution should be interpreted as beams of particles fired at the box from infinity. The beam can either be reflected or transmitted, and so we expect all of *incident*, *reflected* and *transmitted* waves to be present.

What are the matching conditions? As the potential well is finite, the continuity conditions are continuity of both the wavefunction and its first derivative. We therefore require

$$\psi(-a)^+ = \psi(-a)^- \qquad \text{and} \qquad \psi(a)^+ = \psi(a)^-,$$

as well as

$$\frac{\partial\psi}{\partial x}(-a)^+ = \frac{\partial\psi}{\partial x}(-a)^- \qquad \text{and} \qquad \frac{\partial\psi}{\partial x}(a)^+ = \frac{\partial\psi}{\partial x}(a)^-.$$

For bound state solutions with $E < 0$, the wavefunction is exponentially decaying outside the well, with

$$\psi(x) \propto e^{-\kappa|x|}$$

in the regions outside the well.

For positive energy solutions, the wavefunction outside the well is a sum of incident, reflected and transmitted waves

$$\psi(x) = \begin{cases} Ie^{ikx} + Re^{-ikx} & x < 0 \\ Te^{ikx} & x \geq 0 \end{cases} \tag{4.58}$$

Note that in this case (unlike for the step potential example of Eq. 4.50), the wavenumber is the same in both the incident and transmitted regions. This reflects the fact that the potential takes the same value in both regions.

Inside the well, the wavefunction is the sum of two waves,

$$\psi(x) = Ae^{ik'x} + Re^{-ik'x}, \qquad |x| < a, \tag{4.59}$$

with k' set by the depth of the well.

The structure of the solution is now clear. In each separate region of the potential, we solve the Schrödinger equation. We then impose matching conditions for continuity of the wavefunction and its first derivatives at each of these boundaries. This generates a (potentially large) set of simultaneous equations. We then solve these to determine the overall form of the energy eigenstates.

Although conceptually clean, it is important to be precise in solving the simultaneous equations. The problem sheets should provide you with plenty of practice here!

5. The Quantum Harmonic Oscillator

The quantum harmonic oscillator is, together with the Hydrogenic atom, one of the two most important quantum systems. It appears again, and again, and again, throughout physics. It may not be the case that absolutely everything in physics can be approximated as a harmonic oscillator, but quite a number of things can. Is this an accident? Is it the over-confidence of physicists modelling everything as the simplest possible case?

Actually, there is a good reason for the ubiquity of harmonic oscillators. To understand this, we need to think a little bit about perturbation theory. Suppose we have a particle in a general potential, with

$$H = \frac{\hat{p}^2}{2m} + V(\hat{x}). \tag{5.1}$$

In fact, this doesn't even need to be a particle – the above description can apply in any case where the *effective* degrees of freedom of the system reduce to a 1-dimensional coordinate $\hat{x}$.

Minima of the potential $V(\hat{x})$ are non-generic: for almost every value of $\hat{x}$, the potential is not at a minimum. However, dynamics causes a field to roll down a potential, and equilibrium values of $\hat{x}$ are at minima of the potential. Consequently, near equilibrium the potential will look like

$$V(x) = V_0 + \frac{1}{2}kx^2 + \lambda x^3 + \ldots \tag{5.2}$$

For *small* perturbations, the leading term will always be the quadratic one (when x is small enough, x^2 always beats x^3). Even if 'large' explorations would be sensitive to the cubic and quartic terms in the potential, locally the potential close to an equilibrium point looks quadratic (there are more exact and technical ways of making this point, but the key principle is simply that critical points locally look like quadratic).

In here, we find the reason why so much physics, from so many different areas of the subject, can be described as a quantum harmonic oscillator: the quantum harmonic oscillator is the physics of quadratic potentials, and what is needed for it is an equilibrium point locally described as a quadratic. Everywhere, there are harmonic oscillators!

5.1 Solving the Quantum Harmonic Oscillator

The Hamiltonian for the quantum harmonic oscillator is then

$$H = \frac{\hat{p}^2}{2m} + \frac{k\hat{x}^2}{2}. \tag{5.3}$$

As ever, the first task in understanding a quantum mechanical system lies in finding the eigenvalues and eigenstates of the Hamiltonian.

There are two ways of doing this. The most obvious way is to write out the Time-Independent Schrödinger Equation and determine the stationary states as wavefunctions,

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{1}{2}kx^2\right)\psi_n(x)=E_n\psi_n(x). \tag{5.4}$$

This is a differential equation. Go forth, solvers of differential equations, and solve. This course is nor primarily about mathematical methods to solve differential equations (and here I refer you to those courses that are. Instead, I will simply state the result before looking at how we derive it in a much more elegant way.

The result is that the eigenstates of Eq. (5.4) are given by

$$\psi_n(x)=\frac{1}{\sqrt{2^n n!}}H_n\left(\frac{x}{l\sqrt{2}}\right)\frac{1}{\left(2\pi l^2\right)^{1/4}}e^{-\frac{x^2}{4l^2}}, \tag{5.5}$$

with $l=\sqrt{\frac{\hbar}{2m\omega}}$ and H_n the nth Hermite polynomial. The corresponding eigenvalues are

$$E_n=\left(n+\frac{1}{2}\right)\hbar\omega, \qquad n\in\mathbb{Z} \tag{5.6}$$

The form of Eq. (5.5) may appear complex, but at heart there is a clear structure. On the right is the ground-state wavefunction,

$$\psi_0(x)=\frac{1}{\left(2\pi l^2\right)^{1/4}}e^{-\frac{x^2}{4l^2}}, \tag{5.7}$$

which is a Gaussian centred at the origin. This gives the basic envelope structure of all the states, and then the Hermite polynomials adjust this for each of the excited states.

However, what is the best way to solve the harmonic oscillator? The best way to solve the quantum harmonic oscillator is through *ladder operators*, also known as *raising* and *lowering* operators. To introduce them, we first set all the constants in the harmonic oscillator Hamiltonian to unity, so

$$H=\frac{\hat{p}^2}{2}+\frac{\hat{x}^2}{2}. \tag{5.8}$$

For this case, we can then define

$$a=\frac{1}{\sqrt{2}}\left(\hat{x}+i\hat{p}\right), \tag{5.9}$$

$$a^\dagger=\frac{1}{\sqrt{2}}\left(\hat{x}-i\hat{p}\right). \tag{5.10}$$

For the general case, we have (with $\omega = \sqrt{k/m}$)

$$a = \frac{m\omega\hat{x} + i\hat{p}}{\sqrt{2m\hbar\omega}}, \tag{5.11}$$

$$a^\dagger = \frac{m\omega\hat{x} - i\hat{p}}{\sqrt{2m\hbar\omega}}. \tag{5.12}$$

The magic of these operators lie in their commutation operations. We evaluate

$$\left[a, a^\dagger\right] = -\frac{i}{2\hbar}\left[\hat{x}, \hat{p}\right] + \frac{i}{2\hbar}\left[\hat{p}, \hat{x}\right] = 1. \tag{5.13}$$

By mutliplying out the operators, we also obtain

$$H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right). \tag{5.14}$$

The combination $N = a^\dagger a$ is an important one, called the *number operator*, in terms of which we can write

$$H = \hbar\omega\left(N + \frac{1}{2}\right). \tag{5.15}$$

It follows straightforwardly from the definition of N and the commutation relation $\left[a, a^\dagger\right] = 1$ that

$$[N, a^\dagger] = a^\dagger, \qquad [N, a] = -a, \tag{5.16}$$

and so in turn we also have

$$[H, a^\dagger] = \hbar\omega a^\dagger, \qquad [N, a] = -\hbar\omega a. \tag{5.17}$$

What is the significance of this? And why are these operators called ladder operators? It all lies in these commutation relations. Suppose we have an existing eigenstate of the harmonic oscillator Hamiltonian, namely a state $|E\rangle$ with

$$H|E\rangle = E|E\rangle \tag{5.18}$$

Then

$$\begin{aligned} Ha^\dagger|E\rangle &= \left(\left[H, a^\dagger\right] + a^\dagger H\right)|E\rangle & (5.19)\\ &= \left(\hbar\omega a^\dagger + Ea^\dagger\right)|E\rangle & (5.20)\\ &= \left(E + \hbar\omega\right)a^\dagger|E\rangle & (5.21) \end{aligned}$$

and so the state $a^\dagger|E\rangle$ is *also* an eigenstate of the Hamiltonian, except with energy eigenvalue $E + \hbar\omega$ – the energy eigenvalue has been *raised* by an amount $\hbar\omega$. This is why the operator $a^\dagger$ is called a *raising* operator: acting on an eigenstate, it brings it to a new eigenstate in which the energy eigenvalue is increased by $\hbar\omega$.

Exactly the same logic applies to a: and

$$H\left(a|E\rangle\right)=(E-\hbar\omega)a|E\rangle \tag{5.22}$$

which tells us that the lowering operator a reduces the energy eigenvalue by an amount $\hbar\omega$.

At first sight, it appears that we can create an infinite number of states (of arbitrarily high positive or negative energy) through acting with the ladder operators. It looks like we can move as far up, or as far down, the ladder as we like. This seems OK for moving upwards: extremely high momentum particles can exist. It is a problem, however, with moving to negative energies, not least as the Hamiltonian is a sum of squares and so it must be the case that $\langle\psi|H|\psi\rangle\geq 0$ for any state!

But what, exactly, goes wrong with continually acting with the lowering operator? What is the error in the logic that leads to Eq. (5.22)?

Eq. (5.22) is correct. But what Eq. (5.22) does not guarantee is that the state $a|E\rangle$ actually exists – for if $a|E\rangle$ is null, then Eq. (5.22) is satisfied trivially, as both sides are simply null. To investigate this, we need to look at the norm of $a|E\rangle$, namely $\langle E|a^\dagger a|E\rangle$. We evaluate:

$$\begin{aligned}\langle E|a^\dagger a|E\rangle &= \langle E|\left(\frac{H}{\hbar\omega}-\frac{1}{2}\right)|E\rangle\\ &=\left(\frac{E}{\hbar\omega}-\frac{1}{2}\right).\end{aligned} \tag{5.23}$$

From this, we see that when – and only when – $E=\frac{\hbar\omega}{2}$, the state $a|E\rangle$ is actually a null state, and so the lowering operator annihilates the state.

From this, we infer the existence of the harmonic oscillator ground state at $E_{ground}=\frac{\hbar\omega}{2}$. if it were possible to continue lowering the energy indefinitely, then we would obtain negative norm states (which are unphysical). The only consistent case is where the downwards steps of the ladder terminate at $E=\frac{\hbar\omega}{2}$ – the ground state of the harmonic oscillator.

(Note this also excludes the case of in-between energies in the spectrum, say at energies of $(\mathbb{Z}+3/4)\,\hbar\omega$. If the energy does not involve precisely half-integral values of $\hbar\omega$, then we could continue to use the lowering operator and would be led to the contradiction of states with negative norm)

In this way, we now have the spectrum of the quantum harmonic oscillator – one of the most important results in all of physics. The energy spectrum has a ground state at an energy $E = \frac{\hbar\omega}{2}$, which we denote as $|0\rangle$, and then the progressive use of raising operators implies the existence of a tower of states $|n\rangle$, such that the energy of the nth state is given by

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega. \tag{5.24}$$

The normalisation of states (when created by raising/lowering operators) also follows from Eq. (5.23), as we can see that

$$||a|n\rangle||^2 = n, \tag{5.25}$$

and so

$$a|n\rangle = \sqrt{n}|n-1\rangle. \tag{5.26}$$

It similarly follows that

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle. \tag{5.27}$$

In this way we realise that the spectrum of the quantum harmonic oscillator is given by $E_n = \left(n + \frac{1}{2}\right)\hbar\omega, n \in \mathbb{Z}$, by starting with the ground state and continually acting with raising operators. Note that as the raising operator, according to Eq. (5.27), does not turn canonically normalised states into canonically normalised states, we also see that in terms of starting from the ground state and then raising through the states, we in fact have

$$|n\rangle = \frac{1}{\sqrt{n!}}\left(a^\dagger\right)^n|0\rangle., \tag{5.28}$$

There are several interesting points to pick out from this, in particular associated to the ground state energy $E_0 = \frac{\hbar\omega}{2}$.

First, that it is non-zero. In a classical harmonic oscillator, the lowest energy configuration is energy-less : if a classical pendulum has zero amplitude and zero speed, it also has zero energy. This is not true of a quantum pendulum: even the lowest-lying ground state still has energy.

The intuition behind this is the Heisenberg Uncertainty Principle. The Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2. \tag{5.29}$$

The only way for the potential energy to vanish is if the particle is known to be at $x = 0$. But, due to the uncertainty principle, this would require infinite delocalisation in momentum space. Forcing the potential energy to be small is equivalent to forcing the kinetic energy to be large – and vice-versa. The existence of the ground state energy is the compromise forced on us by the uncertainty principle: a minimum of energy that balances out that from the kinetic and potential parts.

5.2 Expectation Values in the Harmonic Oscillator

The construction of the ladder operators enables us to calculate various expectation values for the harmonic operator painlessly, and without having to do large overlap integrals. It follows from the form of the ladder operators in Eq. (5.11) and Eq. (5.12) that we can express the position and momentum operators as

$$\hat{x} = \frac{\sqrt{2m\hbar\omega}}{2m\omega}\left(a + a^\dagger\right), \tag{5.30}$$

$$\hat{p} = -i\frac{\sqrt{m\hbar\omega}}{2}\left(a - a^\dagger\right), \tag{5.31}$$

From this it immediately follows that

$$\langle n|\hat{x}|n\rangle = 0 \tag{5.32}$$

and

$$\langle n|\hat{p}|n\rangle = 0, \tag{5.33}$$

as when we act with a single raising or lowering operator then we have either $\langle n|n+1\rangle = 0$ or $\langle n+1|n\rangle = 0$.

This result should be not surprising. In a harmonic oscillator, the pendulum – or whatever – oscillates about the equilibrium point. We expect it to spend the same amount of time on either side of the equilibrium point, and the symmetry of the problem means that we would expect the expectancy of the position (or momentum) to vanish.

However, if we instead insert $\hat{x}^2$ (or higher even powers of $\hat{x}$ or $\hat{p}$) then we get a non-zero value. In fact, we evaluate

$$\begin{aligned}
\langle n|\hat{x}^2|n\rangle &= \frac{\hbar}{2m\omega}\langle n|\left(a + a^\dagger\right)^2|n\rangle && (5.34)\\
&= \frac{\hbar}{2m\omega}\langle n|aa^\dagger + a^\dagger a|n\rangle && (5.35)\\
&= \frac{\hbar}{2m\omega}\langle n|\left(2n+1\right)|n\rangle. && (5.36)\\
&= \frac{\hbar(n+\frac{1}{2})}{m\omega} && (5.37)
\end{aligned}$$

Likewise,

$$\langle n|\hat{p}^2|n\rangle = \left(n + \frac{1}{2}\right)\hbar m\omega. \tag{5.38}$$

Combining the two, we get

$$\langle n|\hat{x}^2|n\rangle\langle n|\hat{p}^2|n\rangle = \left(n + \frac{1}{2}\right)^2 \hbar^2. \tag{5.39}$$

At this point, we note that as the expectancy of both x and p is zero – $\langle n|x|n\rangle = 0$ and $\langle n|p|n\rangle = 0$, this calculation also tells us that the product of the variances in the nth state is given by

$$(\Delta x)^2 (\Delta p)^2 = \left(n + \frac{1}{2}\right)^2 \frac{\hbar^2}{4}, \tag{5.40}$$

and, in particular, in the ground state we have

$$(\Delta x)(\Delta p) = \frac{\hbar}{2}. \tag{5.41}$$

We therefore see that the ground state *saturates* the Heisenberg uncertainty principle.

5.3 Wavefunctions of the Harmonic Oscillator

With the operator formalism, we can return to the wavefunction formalism, as the ladder operators provide a nice approach to deriving the form of the harmonic oscillator wavefunctions. We have already seen that the ground state is annihilated by the lowering operator,

$$a|0\rangle = 0, \tag{5.42}$$

which implies

$$(m\omega\hat{x} + i\hat{p})|0\rangle = 0. \tag{5.43}$$

If we now write this out in position representation, we have (denoting the ground state wavefunction as $\psi_0(x)$),

$$\left(m\omega x - \hbar\frac{\partial}{\partial x}\right)\psi_0(x) = 0. \tag{5.44}$$

Looking at this, it is easy to see that the solution of this must be of the form

$$\psi_0(x) = Ae^{-\frac{m\omega}{2\hbar}x^2}, \tag{5.45}$$

with A a normalisation constant.

As we have already realised that we can get all the other states by acting multiple times with raising operators, we now understand that we can get the rest of the position-representation wavefunctions through

$$\psi_n(x) = \frac{1}{\sqrt{n!}} \left(\frac{1}{\sqrt{2m\hbar\omega}} \left(m\omega\hat{x} - i\hat{p} \right) \right)^n \psi_0(x), \tag{5.46}$$

providing a constructive method to generate the excited wavefunctions of the harmonic oscillator.

6. Symmetries and Transformations

We now move on to discuss the form of symmetries and transformations in quantum mechanics. Symmetries are one of the deep principles of physics. They permeate the subject and recur in related-but-never-quite-identical forms.

We start with the more general idea of transformations. Transformations are what they say on the tin: they transform one system (and the set of states/kets) into another. Transformations can take many forms, but the simplest ones (which we will largely focus on) are those involving spatial transformations: reflections, translations and rotations.

Having just looked at the harmonic oscillator, this is a good place to start thinking about transformations. The Hamiltonian is

$$H_{SHO} = \frac{p^2}{2m} + \frac{1}{2}kx^2. \tag{6.1}$$

The potential is clearly symmetric under the exchange $x \to -x$. This reflection is called *parity* and we denote its action by $\hat{P}$, the parity operator. Clearly, the effect of acting *twice* with $x \to -x$ returns us to our original position, so we can write $\hat{P}^2 = \mathbb{I}$, where $\mathbb{I}$ is the identity operator.

From the explicit form of the harmonic oscillator wavefunctions, it is also easy to see that the energy eigenstates are all either *odd* or *even* parity. As the wavefunctions all involve the Hermite polynomials, which involve odd powers of x in the $n = 1, 3, 5, \ldots$ states and even powers of x in the $n = 0, 2, 4, \ldots$ states, it follows immediately that under the transformation $x \to -x$, then

$$\hat{P}|n\rangle = (-1)^n |n\rangle. \tag{6.2}$$

If an state starts with well-defined parity, then as the Hamiltonian preserves parity it will remain in a state of well-defined parity throughout the evolution. Associated to the (discrete) symmetry of the equations is a (discrete) conserved quantity: the parity, which can either be even or odd. Of course, states can also be in a superposition of parity eigenstates: but the bigger point is that if the original state has well-defined parity, then this will be conserved under the subsequent evolution of the system.

To those of you alert to the subtle scents of physics, this should remind you of Noether's theorem, the statement in classical mechanics that (continuous) symmetries give rise to conserved quantities. Associated to every continuous symmetry transformation, Noether showed that there exists a conserved quantity: the Noether charge of the system.

Noether's theorem is not directly applicable here. It was derived in the context of classical mechanics, and this is a quantum system. Furthermore, Noether's theorem applies to *continuous* symmetries, and this is a discrete symmetry. And yet....one of the meta-truths of physics is that good ideas keep on giving, well beyond the particular location in which they were first conceived. And Noether's theorem is a good idea: indeed, it is better, a bloody brilliant idea.

Noether's theorem – the idea that there is a deep link between symmetries and conserved quantities – is one of these ideas that keep on giving, that express a deep truth of physics that continues to hold far outside the particular confines of classical mechanics in which it was first formulated. Some concepts – forces, for example – shrink with time and become less and less important. Others remain, reinventing themselves into new forms and new equations. The underlying concept remains while the trappings change.

And here, we see this relation between symmetries and conserved quantities: even though the symmetry is not continuous and we work with quantum mechanics not classical mechanics. Physics keeps on physics-ing, and its best ideas survive all our attempts to tell them when and where they are meant to hold.

6.1 Active and Passive Transformations

At this point it is worth discussing one conceptual aspect of transformations: the distinction between *active* and *passive* transformations. With transformations – especially spatial transformations – we can imagine them happening in two ways. In one ways, we pick up the physical states and transform them: we *change the physical state of the system.* For a spatial translation by a in the x-direction, this would correspond to moving a particle located at position x to position $x + a$, and change the ket $|x\rangle$ to the ket $|x + a\rangle$.

We can imagine another type of transformation, in which we change *coordinates.* Coordinates are something that we as humans put down on a physical system; space does not come with a set of (x, y, z) coordinates placed on it. While we may have a clear notion of up and down, the fundamental laws of physics do not come packaged with a preferred choice of coordinates. In this case, the transformation would not alter the physical state, but would change the coordinates we use to label it. Such a transformation is called a *passive* transformation.

Although in principle we could consider both, here we shall focus only on *active* transformations which alter the physical state of a system: they transform the ket to another, different, ket.

6.2 Unitary Transformations

An important concept in all symmetries and transformations is that of a unitary operator. The notion of a unitary matrix should be familiar from earlier courses. A matrix U is *unitary* if

$$UU^\dagger = \mathbb{I}, \tag{6.3}$$

that is

$$U^\dagger = U^{-1}. \tag{6.4}$$

The same concept applies with operators. An operator U is unitary if $UU^\dagger = \mathbb{I}$.

It immediately follows that unitary operators preserve the norm of a state: they transform physical states into physical states. Given a state $|\phi\rangle$ with $\langle\phi|\phi\rangle = 1$, it follows that

$$||U|\phi\rangle|| = \langle\phi|U^\dagger U|\phi\rangle = 1. \tag{6.5}$$

It also follows straightforwardly that if we transform two states $|\phi\rangle$ and $|\psi\rangle$ through a unitary operator, then we find

$$\langle\phi|\psi\rangle = \langle\phi|U^\dagger U|\psi\rangle = \langle U\phi|U\psi\rangle. \tag{6.6}$$

We therefore see that unitary operators preserve amplitudes and norms of states, and so give precisely the behaviour that we would expect of symmetry transformations. Unitary operators are how we realise (symmetry) transformations.

Unitary operators are (almost all of the time) non-Hermitian. Indeed, we can see that the requirement for a unitary operator U to *also* be Hermitian is that

$$U^2 = \mathbb{I}. \tag{6.7}$$

This is (trivially) satisfied for the identity operator, but there is also a non-trivial case: the parity operator. The parity operator, which acts as $P : \mathbf{x} \to -\mathbf{x}$, is also both Hermitiain and unitary.

Under a transformation, will expectation values changes? Suppose we have an observable $\mathcal{O}$. Consider the expectation value,

$$\langle\mathcal{O}\rangle = \langle\psi|\mathcal{O}|\psi\rangle. \tag{6.8}$$

How does this change under a unitary transformation $\psi \to U|\psi\rangle$? We see that (recall that $U^{-1} = U^\dagger$ for unitary transformations)

$$\langle\psi|\mathcal{O}|\psi\rangle \to \langle\psi|U^{-1}\mathcal{O}U|\psi\rangle. \tag{6.9}$$

We see that expectancy values of an operator will always be preserved if

$$U^{-1}\mathcal{O}U = \mathcal{O}, \tag{6.10}$$

or, equivalently through pre-multiplying by U,

$$[\mathcal{O}, U] = 0. \tag{6.11}$$

It follows that expectancy values of an observable are invariant under a transformation when the observable commutes with the unitary transformation operator U. One particular application of this is to the Hamiltonian: we see that all expectancies of the Hamiltonian are unaltered when the the transformation operator U commutes with the Hamiltonian,

$$[U, H] = 0. \tag{6.12}$$

Although we have so far only discussed general transformations U, there is a close connection between infinitesimal transformations and Hermitian operators. For example, infinitesimal translations are generated by the momentum operator, and infinitesimal rotations are generated by the angular momentum operator. If the infinitesimal generator operator is $\mathcal{O}_i$, then the above statement $[U, H] = 0$ reduces to

$$[\mathcal{O}_i, H] = 0. \tag{6.13}$$

Recall that operators commuting with the Hamiltonian implies that they can be simultaneously diagonalised with the stationary states, and so they are conserved along the motion. We here encounter close connection to Noether's theorem in classical mechanics and also the statements (for those of you who doing S7 Classical Mechanics) that quantities remain conserved when their Poisson bracket (the classical version of the commutator) with the Hamiltonian vanishes.

$$[\mathcal{O}, H] = 0. \tag{6.14}$$

6.3 Translations

Translations are both one of the most important types of transformation and also a useful and simpler prototype of more complex examples, which contain the important concepts but within a calculationally simpler framework. A linear translation moves the point $(x, y, z) \equiv \mathbf{x}$ to $\mathbf{x} + \mathbf{a}$, i.e. is a vector translation by $\mathbf{a}$. Almost by definition, it must take the ket corresponding to a particle located at position $\mathbf{x}$ to that of a ket corresponding to a particle located at position $\mathbf{x} + \mathbf{a}$, namely

$$\hat{T}_{\mathbf{a}}|\mathbf{x}\rangle = |\mathbf{x} + \mathbf{a}\rangle. \tag{6.15}$$

We can also use this to work out how wavefunctions transform under translations. Suppose we have a general state $|\psi\rangle$. Then the wavefunction $\psi(\mathbf{x})$ is given (essentially by definition) as

$$\psi(\mathbf{x}) = \langle \mathbf{x}|\psi\rangle. \tag{6.16}$$

We act with the translation operator $T_{\mathbf{a}}$ on $|\psi\rangle$, to get $|\psi'\rangle = T_{\mathbf{a}}|\psi\rangle$. The new wavefunction is

$$\psi'(\mathbf{x}) = \langle \mathbf{x}|\psi'\rangle = \langle \mathbf{x}|T_{\mathbf{a}}|\psi\rangle. \tag{6.17}$$

Now as $T_{\mathbf{a}}^{-1} = T_{-\mathbf{a}}$ (as the inverse of translating by $\mathbf{a}$ is translating by $-\mathbf{a}$), we have

$$\psi'(\mathbf{x}) = \langle \mathbf{x}-\mathbf{a}|\psi\rangle, \tag{6.18}$$

and so

$$\psi'(\mathbf{x}) = \psi(\mathbf{x}-\mathbf{a}). \tag{6.19}$$

This makes perfect sense if you think about it: as ket are shifted along by $\mathbf{a}$, the new wavefunction at a point $\mathbf{x}$ is set by the old one at point $\mathbf{x}-\mathbf{a}$.

If we want to write $\hat{T}_{\mathbf{a}}$ as a unitary operator $U(\mathbf{a})$, can we obtain a nice expression for it?

We can. In fact, as you grow in experience you may anticipate the form this operator 'has' to take. But, first, let us calculate it. To do so, we use the complete set of momentum operators, $\int d\mathbf{p}|\mathbf{p}|\rangle\langle\mathbf{p}| \equiv \mathbb{I}$.

$$\begin{aligned} |\mathbf{x}+\mathbf{a}\rangle &= \mathbb{I}|\mathbf{x}+\mathbf{a}\rangle, \\ &= \int d^3\mathbf{p}\, |\mathbf{p}\rangle\langle\mathbf{p}|\mathbf{x}+\mathbf{a}\rangle. \end{aligned} \tag{6.20}$$

We have used the relation $\langle\mathbf{p}|\mathbf{x}+\mathbf{a}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{-\frac{i}{\hbar}((\mathbf{x}+\mathbf{a})\cdot\mathbf{p})}$.[3] We can now pull out the part of the exponential involving $\mathbf{x}$ to get

$$\begin{aligned} &= \int d^3\mathbf{p}\, \langle\mathbf{p}|\mathbf{x}\rangle e^{-\frac{i}{\hbar}(\mathbf{a}\cdot\mathbf{p})}|\mathbf{p}\rangle \\ &= \int d^3\mathbf{p}\, \langle\mathbf{p}|\mathbf{x}\rangle e^{-\frac{i}{\hbar}(\mathbf{a}\cdot\hat{\mathbf{p}})}|\mathbf{p}\rangle, \end{aligned} \tag{6.21}$$

where we have replaced the momentum *value* with the momentum *operator* (which we can subsequently just pull out the front, to get)

$$\begin{aligned} |\mathbf{x}+\mathbf{a}\rangle &= e^{-\frac{i}{\hbar}(\mathbf{a}\cdot\hat{\mathbf{p}})} \int d^3\mathbf{p}\, |\mathbf{p}\rangle\langle\mathbf{p}|\mathbf{x}\rangle \\ &= e^{-\frac{i}{\hbar}(\mathbf{a}\cdot\hat{\mathbf{p}})}|\mathbf{x}\rangle. \end{aligned} \tag{6.22}$$

---

[3] Insert derivation

From this we infer that the translation operator is given by

$$\hat{T}_{\mathbf{a}} = e^{-\frac{i}{\hbar}\mathbf{a}\cdot\hat{\mathbf{p}}}. \tag{6.23}$$

So we obtain translation by a large, finite amount $\mathbf{a}$ by exponentiating the momentum operator $\hat{\mathbf{p}}$. If we translate by a infinitesimal amount ϵ, then we instead get

$$\hat{T}_{\epsilon} = 1 - \frac{i}{\hbar}\epsilon \cdot \hat{\mathbf{p}}. \tag{6.24}$$

Is this a surprise?

Maybe yes and no. But the more physics you do, the more the answer is no. What Eq. (6.24) tells us is that an infinitesimal spatial translation is generated by the momentum operator. If we want to translate a state $|\psi\rangle$ by an infinitesimal amount, we do so by using the momentum operator. There is a close connection between spatial translation and momentum: you may have already seen this in the context of Noether's theorem in classical mechanics, where (linear) momentum is the conserved quantity that is present when spatial translation is symmetry.

Here we see another such example of this close connection: the momentum operator is the one that generates infinitesimal spatial translations.

Taylor's theorem revisited

To see how this works in more detail, we can use our understanding of the translation operator to revisit Taylor's theorem. Back when you were in nursery, you learned Taylor's theorem, and the expansion (for some general function $\psi(x)$ – we restrict to one dimension for simplicity)

$$\psi(x-a) = \psi(x) + \left(-a\frac{\partial}{\partial x}\right)\psi(x) + \frac{1}{2!}\left(-a\frac{\partial}{\partial x}\right)^2\psi(x) + \ldots \tag{6.25}$$

Another way to write this is as

$$\psi(x-a) = e^{\left(-a\frac{\partial}{\partial x}\right)}\psi(x), \tag{6.26}$$

or equivalently,

$$\psi(x-a) = e^{\frac{-i}{\hbar}\left(ai\hbar\frac{\partial}{\partial x}\right)}\psi(x), \tag{6.27}$$

which we can indeed write as

$$\psi(x-a) = e^{-\frac{i}{\hbar}\mathbf{a}\cdot\hat{\mathbf{p}}}\psi(x) = \hat{T}_{\mathbf{a}}\psi(x), \tag{6.28}$$

corresponding to the correct transformation of the wavefunction under the active transformation $\mathbf{x} \to \mathbf{x}+\mathbf{a}$ (recall that if a ket is translated by $+\mathbf{a}$, we have $\hat{T}_{\mathbf{a}}\psi_{old}(x) = \psi_{new}(x) = \psi_{old}(x-a)$).

6.4 Rotations

Having discussed translations, we now move onto a discussion of rotations. Given what we have said above about translations and the role of linear momentum, you may already have a sense of what is coming when we discuss rotations. As we replace spatial translations with spatial rotations, so we replace linear momentum with angular momentum. In the same way that the linear momentum operator is the generator of infinitesimal translations, so the angular momentum operator is the generator of infinitesimal rotations.

We focus (without loss of generality) on rotations around the z-axis (the corresponding formulae for rotations around the x- and y-axis will be obvious). For an active rotation about the z-axis by an angle θ, the ket $|x, y, z\rangle$ transforms as

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{6.29}$$

and so for infinitestimal rotations we have

$$x' = x - \theta y, \tag{6.30}$$

$$y' = \theta x + y, \tag{6.31}$$

$$z' = z. \tag{6.32}$$

From this we see that the act of the infinitesimal rotation is equivalent to the translation $T_{(-y\theta, x\theta, 0)}$, and thus we can write the operator for this infinitesimal rotation as

$$1 - \frac{i\theta}{\hbar}\left(-yp_x + xp_y\right) = 1 - \frac{i}{\hbar}\theta L_z, \tag{6.33}$$

where $L_z = xp_y - yp_x$. From this we also infer that finite rotations by an angle θ around the z-axis are given by

$$T_\theta = e^{-\frac{i}{\hbar}\theta L_z} \tag{6.34}$$

We see this is the precise analogue of finite translations being given by exponentiation of the linear momentum operator; finite rotations are given by exponentiation of the angular momentum operator.

For more general rotations, by an angle ϕ about an axis given by the unit vector $\mathbf{n}$ (which in the case above was the z-axis (0,0,1)), the act of rotation is given by the unitary operator

$$U(\phi\mathbf{n}) = e^{-\frac{i}{\hbar}\phi\mathbf{n}\cdot\mathbf{L}} \tag{6.35}$$

where $\mathbf{L} = (L_x, L_y, L_z)$.

6.5 Time Translations and the Heisenberg Picture

So far we have discussed spatial transformations. What about time? Can we sensibly talk about the idea of transformations in time, or time translations? The idea feels related – but not quite the same – as that of translations in space. And this is what it is – related, but not quite the same. A half-sibling, if you like, of the ideas we have already discussed.

The evolution of states forward in time – modulo any uncertainties regarding measurements and wavefunction collapse – is deterministic and entirely fixed by the time-dependent Schrödinger equation,

$$\hat{H}|\psi\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle. \tag{6.36}$$

For a time-independent Hamiltonian, you can verify that, given an initial state $|\psi(t_0)\rangle$, the solution is

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}\hat{H}(t-t_0)}|\psi(t_0)\rangle. \tag{6.37}$$

(For time-dependent Hamiltonians, the solution is

$$|\psi(t)\rangle = \hat{T}\, e^{-\frac{i}{\hbar}\int_{t_0}^{t}\hat{H}(T)dT}|\psi(t_0)\rangle, \tag{6.38}$$

with $\hat{T}$ the time-ordering operator.)

The time evolution means we can associate the idea of 'time translation' with evolution of a state along the (deterministic) path mapped out by the TDSE. That is, we have the notion of an evolution operator,

$$U(t, t_0) = e^{-\frac{i}{\hbar}\hat{H}(t-t_0)} \tag{6.39}$$

which evolves a state forward in time from t_0 to t. This operator is manifestly unitary (as it represents a phase and so $U^\dagger U = 1$) and is often called the *propagator*).

In this way, it becomes useful to think about time evolution as also governed by the action of a unitary operator. This notion of the propagator becomes particularly important once we introduce time-dependent potentials and study scattering, interactions and transitions: but this is the collective Oxford we, as this will not be done by me, but rather in the Further Quantum Mechanics part of the course.

We also use this point to discuss the *Heisenberg Picture* in quantum mechanics. This can be useful in various computations of scattering and time-dependent perturbation theory. In the normal picture, which we work in almost entirely throughout these notes, states evolves in time and operators remain fixed. States evolve according to the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle, \tag{6.40}$$

and so operator expectancy values behave as

$$\langle\mathcal{O}\rangle(t) = \langle\psi(t)|\mathcal{O}|\psi(t)\rangle, \tag{6.41}$$

which we can write out as

$$\langle\mathcal{O}\rangle(t) = \langle\psi(t_0)|U(t,t_0)^\dagger\mathcal{O}U(t,t_0)|\psi(t_0)\rangle. \tag{6.42}$$

However, another way to view this would to regard the states as fixed in time, and operators as evolving: it ultimately gives the same amplitudes. So, in terms of the unitary time evolution operator $U(t,t_0)$, we could say

$$\mathcal{O}(t) = U(t,t_0)^\dagger\mathcal{O}(t_0)U(t,t_0) \tag{6.43}$$

and then regard the evolution of expectancy values as

$$\langle\mathcal{O}\rangle(t) = \langle\psi(t_0)|\mathcal{O}(t)|\psi(t_0)\rangle. \tag{6.44}$$

In this case (in the Heisenberg picture), the operators evolve, not the states. The operator evolution is governed by (given that $U(t,t_0) = e^{-\frac{i}{\hbar}\hat{H}(t-t_0)}$),

$$\frac{d\mathcal{O}(t)}{dt} = \frac{i}{h}\left[H,\mathcal{O}(t)\right]. \tag{6.45}$$

The Heisenberg picture can be useful for the time-evolution of quantum systems with Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$, with $\hat{V}$ a perturbation. In this case, it can be useful to pull out the base evolution associated to $\hat{H}_0$ by going to the Heisenberg picture, allowing us to focus only on the effects of the the perturbation.

7. Angular Momentum and Spin

We now want to discuss in detail angular momentum and the way angular momentum can appear in quantum mechanics. What we are going to do is somewhat analogous to what we did for the harmonic oscillator. We are going to look at the structure of the angular momentum operators $\hat{L}_i = \epsilon_{ijk}\hat{x}_j\hat{p}_k$ and look at how they commute with both each other and with the total angular momentum $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$.

This will reveal the possible allowed structures and values for the angular momentum in quantum mechanics. This ends up as a much more powerful approach than just trying to leap into writing out $L_i = \epsilon_{ijk}\hat{x}_j\hat{p}_k$ in position space coordinates, as this ends up missing one very important feature of angular momentum in quantum mechanics (namely the existence of spin angular momentum with half-integral angular momentum).

Explicitly, the angular momentum operators are

$$L_x = yp_z - zp_y, \tag{7.1}$$

$$L_y = zp_x - xp_z, \tag{7.2}$$

$$L_z = xp_y - yp_x. \tag{7.3}$$

If we compute the commutation of the angular momentum operators with themselves, we obtain

$$[L_i, L_j] = i\hbar\epsilon_{ijk}L_k. \tag{7.4}$$

This can be done either by using the individual forms of L_x, L_y and L_z together with the fundamental position-momentum commutators $[x, p_x] = i\hbar$, etc – or, alternatively, by working with index notation throughout and directly calculating $[L_i, L_j]$ (for this, we need to recall the relation $\epsilon_{iab}\epsilon_{icd} = \delta_{ac}\delta_{bd} - \delta_{ad}\delta_{bc}$). In any case, we end up with

$$[L_x, L_y] = i\hbar L_z, \tag{7.5}$$

$$[L_y, L_z] = i\hbar L_x, \tag{7.6}$$

$$[L_z, L_x] = i\hbar L_y. \tag{7.7}$$

Note that this means that we cannot, in general, simultaneously measure the different components of the angular momentum vector: we cannot, in general, know both L_x and L_y at the same time (the qualification 'in general' is because, in the case where there is no angular momentum, then it is consistent to have $L_x = L_y = L_z = 0$ and us to know all three components of the angular momentum simultaneously).

While L_i does not commute with itself, one object it does commute with is the total angular momentum operator $L^2 = L_x^2 + L_y^2 + L_z^2$. To see this, we note (e.g.)

$$\begin{aligned}[L_x, L_x^2 + L_y^2 + L_z^2] &= [L_x, L_y^2] + [L_x, L_z^2] \\ &= i\hbar(L_z L_y + L_y L_z) - i\hbar(L_y L_z + L_z L_y) \\ &= 0. \end{aligned} \tag{7.8}$$

From this we see that, for any system, we can simultaneouly measure both the *overall* angular momentum as well as *one* of the vector components of angular momentum (conventionally taken to be the z-component).

Angular Momentum and Rotations

It is relatively to see that, for example, $[L_i, \mathbf{x} \cdot \mathbf{x}] = 0$. To do so, we write

$$[L_i, x_i x_i] = \epsilon_{ijk}[\hat{x}_j \hat{p}_k, \hat{x}_m \hat{x}_m] \tag{7.9}$$

$$= \epsilon_{ijk}\hat{x}_j[\hat{p}_k, \hat{x}_m \hat{x}_m] \tag{7.10}$$

$$= \epsilon_{ijk}\hat{x}_j(-2i\hbar\delta_{km})\hat{x}_m \tag{7.11}$$

$$= \epsilon_{ijk}\hat{x}_j\hat{x}_k(-2i\hbar) \tag{7.12}$$

$$= 0, \tag{7.13}$$

where in the last line we have used the fact that ϵ_{ijk} is antisymmetric in all its indices whereas $\hat{x}_j\hat{x}_k$ is symmetric under exchange of indices (and the contraction of antisymmetric and symmetric tensors vanishes).

A similar, almost identical, calculation shows that $[L_i, \mathbf{p} \cdot \mathbf{p}] = 0$. Why is this? Actually, there is a deeper reason to understand why this is the case. The deeper reason comes from thinking back to the connection between the angular momentum operators and rotations. The angular momentum operators are the generators of rotations. Physically, the statement that $[L_i, \mathbf{p} \cdot \mathbf{p}] = 0$ is equivalent to the statement that $\mathbf{p} \cdot \mathbf{p}$ is invariant under rotations – which of course it should be, as $\mathbf{p} \cdot \mathbf{p}$ is a scalar!

Indeed, more generally any scalar object – one which is invariant under rotations – will commute with the angular momentum operator, however complicated its apparent form. The commutation of any object with the angular momentum vector tells us how it transforms under rotations. For a scalar quantity s, we have

$$[L_i, s] = 0, \tag{7.14}$$

whereas for a vector quantity $\mathbf{v_j}$, we have

$$[L_i, \mathbf{v_j}] = i\hbar\epsilon_{ijk}v_k, \tag{7.15}$$

(the factor $i\hbar$ arises from the precise definition of L_i.

7.1 Allowed Values of Angular Momentum

We can use the angular momentum commutation relations

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z, \tag{7.16}$$

$$\left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x, \tag{7.17}$$

$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y, \tag{7.18}$$

together with

$$\left[\hat{L}_i, \hat{L}^2\right] = 0 \tag{7.19}$$

to determine the possible values of angular momentum that can appear in quantum mechanics. To do so, we start by introducing operators $L_\pm = L_x \pm iL_y$. We will see that these behave in a way similar to the ladder operators of the harmonic oscillator, except in terms of raising and lowering the z-component of angular momentum. Let us treat their properties a little more explicitly.

First, it is reasonably easy to see that

$$[L_+, L_z] = [L_x + iL_y, L_z] = -i\hbar L_y - \hbar L_x = -\hbar L_+, \tag{7.20}$$

and likewise

$$[L_-, L_z] = [L_x - iL_y, L_z] = -i\hbar L_y + \hbar L_x = \hbar L_-, \tag{7.21}$$

These commutation relations tell us, analogously to the ladder operators in the harmonic oscillator, that when we act with $L_\pm$ on a state we raise (for $\hat{L}_+$) or lower (for $\hat{L}_-$) the value of $\hat{L}_z$.

In particular, the fact that $\hat{L}^2$ and $\hat{L}_z$ commute means that we can construct a simultaneous eigenbasis of $\hat{L}^2$ and $\hat{L}_z$, in which we can write states as $|\beta, \gamma\rangle$, with β and γ the $\hat{L}^2$ and $\hat{L}_z$ eigenvalues respectively. It then follows that by acting with $L_\pm$ we can raise or lower the L_z eigenvalue,

$$L_\pm|\beta, \gamma\rangle = \alpha_\pm|\beta, \gamma \pm \hbar\rangle \tag{7.22}$$

By progressively acting with $L_\pm$ we can continue to raise (or lower) the L_z eigenvalue until we must reach a point where we annihilate the state. Why must we end up with annihilating the state (recall that in the harmonic oscillator case, the lowering operator ended up annihilating the ground state, but the raising operator can be used indefinitely)?

The easiest way to see this is note that $[\hat{L}^2, L_\pm] = 0$ and the total angular momentum takes the form

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{7.23}$$

The action of the raising/lowering operator does not change the L^2 eigenvalue (as the two operators commute) but it does increase/decrease the L_z eigenvalue. However, the L_z^2 eigenvalue can never get bigger than the L^2 eigenvalue (as L^2 contains L_z^2). Therefore, it follows that the repeated action of $L_\pm$ must terminate. We can raise/lower the L_z eigenvalue so far – but no further.

Where exactly is 'no further'? Here we do something very similar to what we did with the harmonic oscillator. First consider repeated action with the raising operator L_+. When we get to the 'top' state, we know (by definition of what the top state will be), that it will be annihilated by the action of L_+ and so we have

$$L_+|\beta, \gamma_{top}\rangle = 0. \tag{7.24}$$

This implies that the norm of this state vanishes and so we have

$$\langle\beta, \gamma_{top}|L_- L_+|\beta, \gamma_{top}\rangle = 0. \tag{7.25}$$

However, we can also write

$$\begin{aligned}
L_- L_+ &= (L_x - iL_y)(L_x + iL_y) \\
&= (L_x^2 + L_y^2 + i(L_x L_y - L_y L_x) \\
&= (L_x^2 + L_y^2 + L_z^2 - L_z^2 - \hbar L_z), \\
&= \hat{L}^2 - \hat{L}_z^2 - \hbar L_z.
\end{aligned} \tag{7.26}$$

where we have used the commutator $[L_x, L_y] = i\hbar L_z$. Substituting this into Eq.$\tilde{(}$7.25), we obtain

$$\langle\beta, \gamma_{top}|\hat{L}^2 - \hat{L}_z^2 - \hbar L_z|\beta, \gamma_{top}\rangle = 0, \tag{7.27}$$

and so

$$\beta - \gamma_{top}^2 - \hbar\gamma_{top} = 0, \tag{7.28}$$

which we can rewrite as

$$\beta = \gamma_{top}\left(\gamma_{top} + \hbar\right). \tag{7.29}$$

On the other hand, we can repeat everything we have done, except now with the lowering operator.

$$L_-|\beta, \gamma_{bottom}\rangle = 0. \tag{7.30}$$

This implies that the norm of this state vanishes and so we have

$$\langle\beta, \gamma_{bottom}|L_+L_-|\beta, \gamma_{bottom}\rangle = 0. \tag{7.31}$$

However, we can also write

$$\begin{aligned} L_+L_- &= (L_x + iL_y)\,(L_x - iL_y) \\ &= (L_x^2 + L_y^2 - i(L_xL_y - L_yL_x) \\ &= (L_x^2 + L_y^2 + L_z^2 - L_z^2 + \hbar L_z), \\ &= \hat{L}^2 - \hat{L}_z^2 + \hbar L_z. \end{aligned} \tag{7.32}$$

where we have used the commutator $[L_x, L_y] = i\hbar L_z$. Substituting this into Eq.~(7.31), we obtain

$$\langle\beta, \gamma_{bottom}|\hat{L}^2 - \hat{L}_z^2 + \hbar L_z|\beta, \gamma_{bottom}\rangle = 0, \tag{7.33}$$

and so

$$\beta - \gamma_{bottom}^2 + \hbar\gamma_{bottom} = 0, \tag{7.34}$$

which we can rewrite as

$$\beta = \gamma_{bottom}\,(\gamma_{bottom} - \hbar)\,. \tag{7.35}$$

Comparison of Eqs. (7.29) and (7.35) shows that, to satisfy them both, we need

$$\gamma_{bottom} = -\gamma_{top}. \tag{7.36}$$

Furthermore, we also know that γ_{bottom} and γ_{top} must be separated by integer units of $\hbar$, as the raising/lowering operator changes the z angular momentum quantum number by $\hbar$. Putting these two facts together, the only possible values for γ_{top} involves integral or half-integral values of $\hbar$. That is,

$$\gamma_{top} \in \frac{n\hbar}{2}, \qquad n \in \mathbb{Z}. \tag{7.37}$$

This argument does not say what γ_{top} should be for any particular system: but what it does tell us is that these are the *only possible allowed* values that angular momentum can take.

At this point, we have enough to shift to the conventional notation for angular momentum states, namely

$$|l, m\rangle,$$

where l can be integer or half-integer and shows the total angular momentum, with the L^2 eigenvalue being $l(l+1)\hbar^2$, whereas m can run between $-l$ and l, with the L_z eigenvalue given by $m\hbar$.

Note that the above arguments are very general: they tell us, from first principles, what the only possible allowed values for quantum-mechanical angular momentum are: whatever the system, it *must* fit into this structure.

In terms of this general structure, we have

$$\begin{aligned} \hat{L}^2|l,m\rangle &= l(l+1)\hbar^2|l,m\rangle, & (7.38)\\ \hat{L}_z|l,m\rangle &= m\hbar|l,m\rangle, & (7.39)\\ \hat{L}_\pm|l,m\rangle &= \hbar\sqrt{l(l+1)-m(m\pm 1)}|l,m\pm 1\rangle. & (7.40) \end{aligned}$$

We reiterate here that picking out the z direction is with complete loss of generality: while we choose to align around the z-axis, there is clearly no law of nature that selects the z-axis. We could equally well have expressed the angular momentum basis in terms of eigenstates of L_x or L_y: but convention tells us that we use L_z.

The above was general, and covers all realisations of angular momentum. We now start looking at specific examples of angular momentum.

Matrix Description for $l = 1$

We now apply the above formalism to determine the matrix representation of the angular momentum operators for the case of $l = 1$ (i.e. one unit of angular momentum). This system has three states, corresponding to $m = 1$, $m = 0$ and $m = -1$. We can represent these three states as vectors (for $m = 1$, $m = 0$, $m = -1$ respectively),

$$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \qquad \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \qquad \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

The matrix representation of $\hat{L}_z$ is immediate (as $\hat{L}_z|l,m\rangle = m\hbar|l,m\rangle$):

$$\hat{L}_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \qquad (7.41)$$

To find the matrix representation of $\hat{L}_x$ and $\hat{L}_y$, we use the fact that $L_\pm = L_x \pm iL_y$, and so $L_x = \frac{1}{2}(L_+ + L_-)$ and $L_y = -\frac{i}{2}(L_+ - L_-)$. We then combine these the action of the $L_\pm$ in Eqs. (7.38), to obtain

$$L_+ = \hbar \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix}, \qquad L_- = \hbar \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix}, \tag{7.42}$$

giving

$$L_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \qquad L_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}. \tag{7.43}$$

We now move to consider the representation of angular momentum in position space.

7.2 Angular Momentum in Position Space

We can also write out the angular momentum operators in position space, in the langauge of wavefunctions. Indeed, in many ways this would have seemed the natural point to start at. Rather than go through the analysis of the previous subsection, why not just write out the angular momentum operators as differential operators, and see what the corresponding eigenfunctions and eigenvalues?

Although natural, this ends up missing a heffalump-sized subtlety: most of the universe. This approach manages to miss out on spin, the case of $\hbar/2$ of angular momentum – the value that applies for the electrons, quarks, protons, neutrons that make up us. But what happens if we are unsubtle, and what goes wrong?

The angular momentum operators are

$$L_x = yp_z - zp_y, \tag{7.44}$$

$$L_y = zp_x - xp_z, \tag{7.45}$$

$$L_z = xp_y - yp_x. \tag{7.46}$$

If we write them out in position space, we have

$$\begin{aligned} L_x &= -i\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right), \\ L_y &= -i\hbar \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right), \\ L_z &= -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right). \end{aligned} \tag{7.47}$$

However, the reason for working with angular momentum operators is that the system has some form of natural rotational symmetry. For such cases, x, y and z coordinates conceal rather than clarify this structure. They are not wrong as such: but they are not right either.

Instead, we want to work with coordinates adapted to the angular symmetries of the problem. For spherical symmetries, the natural such coordinates are (r, θ, ϕ) coordinates. These are related to (x, y, z) coordinates by

$$x = r \sin\theta \cos\phi, \tag{7.48}$$
$$y = r \sin\theta \sin\phi, \tag{7.49}$$
$$z = r \cos\theta. \tag{7.50}$$

Converting the $\frac{\partial}{\partial x_i}$ derivatives into polar coordinate derivatives is an exercise in the chain rule. Substituting into the relations of Eq. (7.47), we find

$$L_x = -i\hbar \left[-\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right] \tag{7.51}$$
$$L_y = -i\hbar \left[\cos\phi \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right] \tag{7.52}$$
$$L_z = -i\hbar \frac{\partial}{\partial\phi} \tag{7.53}$$

Combining these, we can also get the total angular momentum operator,

$$\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial^2\phi} \right] \tag{7.54}$$

As $[\hat{L}^2, \hat{L}_i] = 0$, we can simultaneously diagonalise the total angular momentum and also any one of the vector components of angular momentum. Conventionally, this is $\hat{L}_z$. We can then obtain the simultaneous eigenfunctions and eigenvalues of $\hat{L}^2$ and $\hat{L}_z$ by solving

$$\begin{aligned} \hat{L}^2 Y_{lm}(\theta, \phi) &= l(l+1)\hbar^2 Y_{lm}(\theta, \phi), \\ \hat{L}_z Y_{lm}(\theta, \phi) &= m\hbar Y_{lm}(\theta, \phi). \end{aligned} \tag{7.55}$$

We use here the conventional notation $Y_{lm}(\theta, \phi)$ for these eigenfunctions (matching onto the notation of $|l, m\rangle$. These are called the *spherical harmonics* and their precise form can be found by solving the appropriate differential equation. They are normalised as

$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} |Y_{lm}(\theta, \phi)|^2 \sin\theta \, d\theta \, d\phi = 1 \tag{7.56}$$

You are expected to know the form of the $l = 0$ and $l = 1$ spherical harmonics. The $Y_{00}(\theta, \phi)$ harmonic is constant: almost by definition, the absence of any angular momentum means that the state must be entirely invariant under rotation. This then implies

$$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}. \tag{7.57}$$

It should also be clear that, as $\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$, the ϕ dependence of any $Y_{lm}(\theta, \phi)$ is simple:

$$Y_{lm}(\theta, \phi) \propto e^{im\phi}. \tag{7.58}$$

The θ dependence, however, can only be obtained by solving the differential equation explicitly.

Doing this, we find

$$Y_{11}(\theta, \phi) = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi}, \tag{7.59}$$

$$Y_{10}(\theta, \phi) = \sqrt{\frac{6}{8\pi}} \cos\theta, \tag{7.60}$$

$$Y_{1-1}(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\phi}. \tag{7.61}$$

Note that overall phases are entirely conventional, as there is no physical meaning attached to the overall phase of the eigenfunction.

One thing to be aware of with these eigenfunctions is the different normalisation constant between the $Y_{1\pm1}$ and Y_{10} states (this is something students sometimes trip up on).

In a similar vein, the higher spherical harmonics $Y_{lm}(\theta, \phi)$ can all be determined. These spherical harmonics occur ubiquitously in all problems with some (at least approximate) spherical symmetry; one particular example we will come to is that of the Hydrogen atom. In advance of this, note that the degeneracy of the l angular momentum quantum number (the number of m values it supports) is $(2l + 1)$.

There is also a *deep* and *important* point to realised about the position-space description of angular momentum through differential operators, i.e. describing angular momentum via wavefunctions. A wavefunction is a function on space, and as such has to be single-valued. This may seem innocuous but it has a deep implication. As the ϕ dependence of a wavefunction is $Y_{lm}(\theta, \phi) \propto e^{im\phi}$, and the wavefunction must be single-valued, it follows that m must be an integer (*not* a half-integer).

What does this tell us? It tells us that orbital angular momentum, of the type that is the quantum version of a particle rotating around a central point, can only give us integer-quantised angular momentum. However, our general treatment of angular momentum in section 7.1 revealed that half-integral values should also be possible. Where do these come from? The half-integral values of angular momentum are associated to intrinsic angular momentum, called *spin angular momentum*. We now discuss this.

8. Spin and Composite Systems

8.1 Spin systems

We now want to focus in a little more detail on spin-1/2 systems: first in and of themselves, and then later looking at what happens when we combine two spin-1/2 systems. Spin-1/2 systems are important because (almost) all fundamental particles – but especially the electron – have spin-1/2.

Fortunately, we have already done most of the legwork in section 7.1: this covers the general case, and the example of spin-1/2 can be treated as a specific case of the above, restricted to $S = 1/2$.

In particular, the system consists of two states, one with z-angular momentum $+\frac{1}{2}\hbar$ and the other with z-spin $-\frac{1}{2}\hbar$. There are various ways these states are denoted – you should be familiar with them. One way is as 'up' and 'down' states,

$$|\uparrow\rangle \quad \text{and} |\downarrow\rangle.$$

Another way is through 2-component vectors (as there is a basis of 2 states),

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \equiv |\uparrow\rangle, \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix} \equiv |\downarrow\rangle.$$

And finally, in terms of the more geneal formalism,

$$|1/2, +1/2\rangle, \quad |1/2, -1/2\rangle.$$

As the general formalism of angular momentum applies, we can construct the total angular operator $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$ and raising and lowering operators

$$S_\pm = S_x \pm iS_y, \tag{8.1}$$

with

$$S^2|1/2, \pm 1/2\rangle = \hbar^2 1/2(1/2+1)|1/2, \pm 1/2\rangle, \tag{8.2}$$

and

$$S_\pm|s, s_z\rangle = \hbar\sqrt{s(s+1) - s_z(s_z+1)}|s, s_z \pm 1\rangle \tag{8.3}$$

We can construct explicit representations of the spin angular momentum operators using the *Pauli spin matrices.* These are

$$S_i = \frac{\hbar}{2}\sigma_i, \tag{8.4}$$

with

$$[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k, \tag{8.5}$$

and

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

We can write the state of a general spin-1/2 system as $\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \equiv \alpha|\uparrow\rangle + \beta|\downarrow\rangle$. Under rotations, these transform (through the same general logic given in section 7.1),

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \rightarrow e^{\frac{i}{\hbar}\theta\mathbf{n}\cdot\mathbf{S}} \begin{pmatrix} \alpha \\ \beta \end{pmatrix},$$

for a rotation by an angle θ about the axis given by $\mathbf{n}$.

For the particular case of a rotation by θ about the z-axis, this gives

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \rightarrow e^{\frac{i}{\hbar}\theta S_z} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}.$$

Given the form of S_z, it is easy to see that this implies that a rotation of 2π about the z-axis results in the phase of the spinor being multiplied by $e^{\frac{1}{2}\times 2\pi i}$ – which equals -1, not 1.

This is an important and deep point about spin 1/2 (spinor) systems. It ties to the Pauli exclusion principle and represents a deep and subtle truth about nature, so you should not try and skip over this point. On a rotation by 2π, a spin state returns not to itself, but to minus itself. Is this a problem?

Although it feels like it should be a problem (*of course* things return to themselves if you rotate by 2π, common sense tells you!), careful thought ends up showing that this is consistent. Recall that in quantum mechanics it is not the absolute value of wavefunctions (in a generalised sense that includes spinors) that matters. Instead, states enter through amplitudes $\langle\psi|\phi\rangle$ or through expectancy values $\langle\psi|\mathcal{O}|\psi\rangle$ – and all of *these* are invariant when hte individual bras and kets are multiplied by minus signs.

We make a final comment about spinors. Although it is conventional to work in a basis in which S_z is diagonal, and so the two basis states $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ represent states with spin either aligned or anti-aligned with the z direction,[4] However, there is no law of nature telling us what axes we should use, and we can equally well pick any other set of axes.

To find the corresponding pair of states which are aligned (or anti-aligned) along a direction $\mathbf{n}$, we solve for

$$\mathbf{n} \cdot \mathbf{S} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \pm \frac{\hbar}{2} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}. \tag{8.6}$$

Doing so, we obtain the corresponding ket vectors for a spin-1/2 system aligned (or anti-aligned) along the $\mathbf{n}$ direction.

8.2 Composite Systems and Entanglement

Spin is important as many particles (in particular, electrons) have an internal (angular momentum) degree of freedom: **spin**, the $|\uparrow\rangle$ and $|\downarrow\rangle$ states. However, electrons *also* have position space degrees of freedom and so overall we have to combine the two: creating a composite system, with both spin and position degrees of freedom.

Overall, the electron state has to be represented as:

$$|\text{electron}\rangle = |\text{position space}\rangle \otimes |\text{spin}\rangle,$$

which we can schematically write as

$$\Psi(x, y, z) \otimes |\uparrow\rangle.$$

To specify the full state of an electron, we need both position and spin.

This is an example of a *composite* system. Composite systems appear in many parts of quantum mechanics. When learning about them for the first time, it is quite common for them to appear harder than they actually are. Suppose we have two separate quantum systems A and B,

$$A \rightarrow \text{basis of kets } \{|\psi_i\rangle\}$$
$$B \rightarrow \text{basis of kets } \{|\phi_j\rangle\}$$

For the composite (product) system, we have

$$A \otimes B \rightarrow \text{basis of kets } \{|\psi_i\rangle \otimes |\phi_j\rangle\}$$

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[4] To be clear, this is pronounced 'zed'-direction. Not 'zee'-direction.

There are various choices of notation for how we write the basis of the composite system. Examples are

$$|\psi_i\rangle|\phi_j\rangle \quad \text{or} \quad |\psi_i, \phi_j\rangle$$

Generally, the composite system comes from bolting together two separate quantum mechanical systems, each with a space of kets which we label as $|\psi\rangle$ (for the first system) and $|\phi\rangle$ (for the second system). The composite system comes from bolting these together – taking the tensor product of the two spaces, so that the resulting state space can be written as

$$|\psi, \phi\rangle = |\psi\rangle \otimes |\phi\rangle. \tag{8.7}$$

This is also a Hilbert space, and the dimensionality of the composite system is the product of the dimensionality of the two individual systems,

$$\dim\left(|\psi, \phi\rangle\right) = \dim\left(|\psi\rangle\right) \times \dim\left(|\phi\rangle\right) \tag{8.8}$$

The language of tensor products of Hilbert spaces can sometimes hinder rather than help. As a sense check on the dimensionality, note that it is nothing more complex than a primary school problem of the nature, 'Q. Amy has to pick one number between 0 and 9 and one letter from A to Z. How many total options are there? A. 260'

Some examples of composite systems $|A\rangle \otimes |B\rangle$:

1. **Electron:**

$$\begin{aligned} A &\rightarrow \text{position wavefunction} \\ B &\rightarrow \text{internal spin} \end{aligned}$$

2. **Spin system:**

$$\begin{aligned} A &\rightarrow |\text{spin } 1/2\rangle \\ B &\rightarrow |\text{spin } 1/2\rangle \end{aligned}$$

3. **Positions:**

$$\begin{aligned} A &\rightarrow |\text{position of particle 1}\rangle \\ B &\rightarrow |\text{position of particle 2}\rangle \end{aligned}$$

Given that the composite system is formed from the tensor product of two separate Hilbert spaces, we can (as stated above) form a basis of states for the composite system from the product states of the basis states of the individual systems, i.e.

$$|\psi_i\rangle \otimes |\phi_j\rangle$$

Any state of the composite system can be expressed as a linear combination of these product states. *However* – the fact that every state can be expressed as a linear combination of product states does *not* mean that every state *is* a product state. This leads us to a simple, but important, definition:

In a composite system, a state is said to be *entangled* if it cannot be written as a product state $|\psi_a\rangle \otimes |\phi_b\rangle$ (note that $|\psi_a\rangle$ can refer to any state vector in $|\psi\rangle$, not only basis vectors).

The language 'entangled' arises because, in an entangled state of the composite system, the state of system 1 depends on the state of system 2, and vice-versa. The two systems are tied together.

Note also that it is the state that is entangled, not the system. The property of entanglement applies to the state, not the system. There are states of the composite system that are product states and so are not entangled. The *composite system*, by itself, is not entangled – that is a property of some of the states.

Operators on Composite States

In composite systems, the simplest way of forming operators acting on the whole composite system is through the sum of an operator acting on the first system plus an operator acting on the second. For example, if we have individual Hamiltonians H_1 and H_2, we can construct a composite Hamiltonian

$$H = H_1 + H_2 \tag{8.9}$$

The action of H on a general composite state $|\psi\rangle \otimes |\phi\rangle$ is given by

$$H|\psi\rangle \otimes |\phi\rangle = (H_1 + H_2)\,|\psi\rangle \otimes |\phi\rangle = (H_1|\psi\rangle) \otimes |\phi\rangle + |\psi\rangle \otimes (H_2|\phi\rangle)\,. \tag{8.10}$$

Note that, even though the initial state is a product state and the Hamiltonian is a simple linear sum, the action of the Hamiltonian creates (in general) a non-product state, namely an *entangled* state.

As time-evolution of states is governed by the Hamiltonian through $e^{-\frac{i}{\hbar}H(t-t_0)}$, note that this implies that (in general) time evolution will introduce entanglement into the system even if the original state was a pure product state.

Spin Systems and Entanglement

One of the simplest cases of entanglement arises in the spin systems we have already studied. When we combine two spin-1/2 systems, there are four possible states of the composite system,

$$|\!\uparrow\rangle \otimes |\!\uparrow\rangle, \quad |\!\uparrow\rangle \otimes |\!\downarrow\rangle, \quad |\!\downarrow\rangle \otimes |\!\uparrow\rangle, \quad |\!\downarrow\rangle \otimes |\!\downarrow\rangle,$$

I will choose a slightly different basis for these states (we will see below, in our discussion of the combination of angular momentum, why these are the natural choice). In this new basis, this set of four states combine naturally into the symmetric triplet (which – we shall see – represent the spin 1 $S = 1$ composition) and the antisymmetric singlet (likewise, the spin 0 $S = 0$ composition), as

$$\left\{ |\!\uparrow\rangle \otimes |\!\uparrow\rangle, \frac{1}{\sqrt{2}} \left(|\!\uparrow\rangle \otimes |\!\downarrow\rangle + |\!\downarrow\rangle \otimes |\!\uparrow\rangle \right), \quad |\!\downarrow\rangle \otimes |\!\downarrow\rangle, \right\}, \left\{ \frac{1}{\sqrt{2}} \left(|\!\uparrow\rangle \otimes |\!\downarrow\rangle - |\!\downarrow\rangle \otimes |\!\uparrow\rangle \right) \right\}.$$

However, two of these states are *entangled* states, namely

$$\frac{1}{\sqrt{2}} \left(|\!\uparrow\rangle \otimes |\!\downarrow\rangle + |\!\downarrow\rangle \otimes |\!\uparrow\rangle \right)$$

and

$$\frac{1}{\sqrt{2}} \left(|\!\uparrow\rangle \otimes |\!\downarrow\rangle - |\!\downarrow\rangle \otimes |\!\uparrow\rangle \right).$$

For both entangled states, we can see that, while there is a fifty per cent chance of finding both the first and second system in either the up or down state, measuring the first system tells us precisely the state of the second system (and vice-versa).

Note also the crucial difference in the relative sign of the two states: while both states have $S_z = 0$, the first state corresponds to overall $S = 1$ whereas the second state corresonds to the overall $S = 0$ combination.

Entanglement in Position Space

Suppose we have a system of two particles. Treated by themselves, each would be a single quantum mechanical system with a space of wavefunctions. However, in the composite system we want to have a *single* state that represents *both* particles. We consider the position wavefunctions:

$$\psi_A(x_A), \quad \psi_B(x_B)$$

where A and B represent two different quantum systems, with individual basis kets $|x_A\rangle$ and $|x_B\rangle$.

In a composite system, the basis kets would now be written as:

$$|x_A, x_B\rangle$$

while the general composite wavefunction is:

$$\Psi(x_A, x_B).$$

The composite wavefunction *may* be a product of individual wavefunctions, $\Psi(x_A, x_B) = \psi_1(x_A)\psi_2(x_B)$ but it is **not necessarily** a product of individual wavefunctions, and in general

$$\Psi(x_A, x_B) \neq \psi_1(x_A)\psi_2(x_B)$$

Looking ahead to the Further Quantum course, when these examples will appear in more depth, we consider the case of two particles in an infinite potential well, for which we can label the single-particle eigenfunctions as:

$$\psi_0, \psi_1, \psi_2, \psi_3, \ldots$$

for the ground state, first excited state, second excited state, etc.

Suppose we now want to consider the energy states of the *composite* system with *two* (non-interacting) identical particles in the potential well.[5] The ground state of the composite system will have both particles in the ground state, with the energy eigenfunction for the **ground state** of the composite system being given by:

$$\Psi(x_A, x_B) = \psi_1(x_A)\psi_1(x_B)$$

which is a **symmetric** product state.

After the ground state, we can then consider the first excited state(s). These are degenerate (with degeneracy two). In terms of product states, one possible state is

$$\psi_1(x_A)\psi_2(x_B)$$

whereas another possibility is

$$\psi_2(x_A)\psi_1(x_B).$$

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[5] For the moment, we ignore questions of Bose symmetry and the Pauli exclusion principle. In Further Quantum, you will see the consequences when the Pauli exclusion principle is applied, requiring that the overall wavefunction of systems of identical fermions has to be antisymmetric under particle exchange.

While these are product states, we can also express them as symmetric and antisymmetric combinations:

$$\frac{1}{\sqrt{2}}\left(\psi_1(x_A)\psi_2(x_B) \pm \psi_2(x_A)\psi_1(x_B)\right).$$

In this case,

- $+$ corresponds to a **symmetric** state.
- $-$ corresponds to an **antisymmetric** state.

Written as such, these states are *entangled*. You will see more of them later in the Further Quantum Course.

8.3 Combining Angular Momentum

A common and useful example of composite systems comes when we have to combine two separate sources of angular momentum. This occurs when we deal with system with two separate sources of angular momentum which can take independent values, denoted as $\mathbf{J}_1$ and $\mathbf{J}_2$, and we want to express states in terms of the combined (total) angular momentum operator $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$.

One particularly common example of this involves the electron in an atom. The electron has orbital angular momentum associated to its position space wavefunction. It also has spin angular momentum, associated to the intrinsic nature of being an electron. In principle, these two aspects of angular momentum are independent, and so we can define a *total* angular momentum by combining the orbital and spin angular momenta of the electron In this case,

- $\mathbf{J}_1$ represents the orbital angular momentum $\mathbf{L}$.
- $\mathbf{J}_2$ represents the spin angular momentum $\mathbf{S}$.

and the total angular momentum is given by:

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

Another example would be when we want to consider the total angular momentum of an atom, and we need to combine the angular momentum of the nucleus with the angular momentum of the electron. Note that as a general nucleus consists of many protons and neutrons, their combined spins can add up to give a nuclear angular momentum much larger than 1/2. In this case, we can have

$$\mathbf{J}_{atom} = \mathbf{J}_{nucleus} + \mathbf{J}_{electron}$$

When thinking about combining angular momentum in this way, we will always assume (and it will always be the case) that the two separate forms of angular momentum commute with each other: that is, we can measure them both at the same time. If $\mathbf{J}_1$ and $\mathbf{J}_2$ are the two angular momenta we combine, then

$$[\mathbf{J}_1, \mathbf{J}_2] = 0$$

and so each can be measured simultaneously.

Composite Angular Momentum States

The composite angular momentum system comes from bolting together the two separate angular momentum system. Doing so, we get a set of basis states for the resulting composite system:

$$|j_1, m_1\rangle \otimes |j_2, m_2\rangle$$

The total number of states in the composite system is given by:

$$(2j_1 + 1)(2j_2 + 1),$$

where j_1 is the total angular momentum of system 1 and j_2 is the total angular momentum of system 2. What we want to understand is how to group these states so that they are eigenstates of the total angular momentum operator $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$ and its square $\mathbf{J}^2$.

As $\mathbf{J}$ is constructed as the sum of two separate angular momenta,

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2,$$

it follows that $\mathbf{J}$ also obeys the angular momentum commutation relations,

$$[\mathbf{J}_i, \mathbf{J}_j] = i\hbar\epsilon_{ijk}J_k,$$

and therefore also

$$[\mathbf{J}^2, \mathbf{J}_z] = 0.$$

There is a useful identity to note at this point. As

$$(\mathbf{J}_1 + \mathbf{J}_2)^2 = \mathbf{J}_1^2 + \mathbf{J}_2^2 + 2\mathbf{J}_1 \cdot \mathbf{J}_2,$$

and since $\mathbf{J}_1$ and $\mathbf{J}_2$ commute, it follows that we can express the dot product as:

$$2\mathbf{J}_1 \cdot \mathbf{J}_2 = \mathbf{J}^2 - \mathbf{J}_1^2 - \mathbf{J}_2^2$$

which leads to:

$$\mathbf{J}_1 \cdot \mathbf{J}_2 = \frac{1}{2}\left(\mathbf{J}^2 - \mathbf{J}_1^2 - \mathbf{J}_2^2\right)$$

This identity is useful as it is often the case that the Hamiltonian involves a coupling term

$$\mathbf{J}_1 \cdot \mathbf{J}_2.$$

One example is a spin-orbit coupling $\mathbf{L} \cdot \mathbf{S}$ which occurs in the Hydrogen atom related to the magnetic dipole moments associated to angular momenta (and you shall study in the Further Quantum course).

The fact that $\mathbf{J}$ obeys the angular momenta commutation relations means that it will be possible (i.e. we can find a basis) to expand all the composite states in a basis:

$$|j, j_z\rangle$$

where j is the total angular momentum quantum number. How do we find this basis?

In working this out, it is useful to think back to the set of two spin-1/2 particles. At this point, I just want to *state* how things work out for these (the case where $j_1 = j_2 = 1/2$). These combine into singlet ($j = 0$) and triplet ($j = 1$) states.

$$\begin{aligned}
|1, 1\rangle &= |\uparrow\uparrow\rangle \\
|1, 0\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\
|1, -1\rangle &= |\downarrow\downarrow\rangle \\
|0, 0\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)
\end{aligned}$$

The (mostly serious) reason for doing this is that problems are often easier when you already know the answer: in particular, if you constantly refer to this case of two spin 1/2 particles during the general discussion, it will hopefully make it easier to understand the general account of what is going on.

Organization of States

Among all the basis states $|j_1, m_1\rangle \otimes |j_2, m_2\rangle$, the highest value of z angular momentum can be obtained from the state:

$$|j_1, j_1\rangle|j_2, j_2\rangle$$

This state clearly has:

$$m_z = j_1 + j_2.$$

From the general discussion of angular momentum (and the fact that $\mathbf{J}$ is an angular momentum operator) we know that the states can be organised by total angular momentum j. The state $|j_1, j_1\rangle|j_2, j_2\rangle$ has the highest z value of angular momentum and so must correspond to a state with

$$j = j_1 + j + 2.$$

The general theory of angular momentum now tells us that it is possible to find a set of (linear combinations of) the basis states $|j_1, m_1\rangle \otimes |j_2, m_2\rangle$ such that they correspond to a state of total angular momentum $J = j_1 + j_2$ which pick out the various elements

$$|j_1 + j_2, m\rangle$$

with m running from $-(j_1 + j_2)$ to $(j_1 + j_2)$. This grouping contains a total number of states given by:

$$2(j_1 + j_2) + 1.$$

What is the explicit form of the various states in the $|j_1 + j_2, m\rangle$ mutliplet? In principle (practice), if we want to construct the other $|j_1 + j_2, m\rangle$ states we do so by acting with the lowering operator (exactly analogous to the L_- operators we previously saw in our general account of angular momentum)

$$J_- = J_{1,-} + J_{2,-}.$$

Starting from the highest weight state:

$$|j_1 + j_2, j_1 + j_2\rangle$$

we apply the lowering operator iteratively:

$$J_-|j_1 + j_2, j_1 + j_2\rangle = \hbar\sqrt{(j_1 + j_2)(j_1 + j_2 + 1) - (j_1 + j_2)(j_1 + j_2)}|j_1 + j_2, j_1 + j_2 - 1\rangle,$$

and so by repeated action (and being carefuly with normalisation) we can find all the states of the form $|j_1 + j_2, m\rangle$, ending up with the bottom state

$$|j_1 + j_2, -(j_1 + j_2)\rangle.$$

This fills out the states of the form $|j_1 + j_2, m\rangle$. What about other states? Recall we started with $|j_1, j_1\rangle \otimes |j_2, j_2\rangle$, which was the *only* state with $m = j_1 + j_2$, giving the top state

$$|j_1 + j_2, j_1 + j_2\rangle.$$

However, below this, we have *two* states with $m = j_1 + j_2 - 1$. These can can be written as linear combinations of

$$|j_1, j_1\rangle|j_2, j_2 - 1\rangle \quad \text{and} \quad |j_1, j_1 - 1\rangle|j_2, j_2\rangle.$$

These states combine as symmetric and antisymmetric combinations, with (neglecting normalisations for the moment)

$$|j_1, j_1\rangle|j_2, j_2 - 1\rangle \pm |j_1, j_1 - 1\rangle|j_2, j_2\rangle.$$

The *symmetric* combination is associated to $J_-|j_1, j_1\rangle \otimes |j_2, j_2\rangle = (J_{1,-} + J_{2,-})|j_1, j_1\rangle \otimes |j_2, j_2\rangle$ and corresponds to the state $|j_1 + j_2, j_1 + j_2 - 1\rangle$.

What about the other state? This is itself now the 'highest-z-value' state of a grouping, and so must corresond to (and indeed does correspond to) the top state of an angular momentum multiplet with $j = (j_1 + j_2 - 1)$:

$$|j_1 + j_2 - 1, j_1 + j_2 - 1\rangle.$$

Progressively acting on *this* state with J_- then also fills out an angular momentum multiplet with:

$$j = j_1 + j_2 - 1$$

and multiplicity

$$2(j_1 + j_2 - 1) + 1,$$

ending with the bottom state $|j_1 + j_2 - 1, -(j_1 + j_2 - 1)\rangle$.

In a very similar way, we can now realise that there are *three* independent states with z-angular momentum $j_1 + j_2 - 2$. Two of these we have already tracked down, as belonging to multiplets with $j = j_1 + j_2$ and $j = j_1 + j_2 - 1$. The third we now identify as the top state of a multiplet with $j = j_1 + j_2 - 2$.

In this way, we continue this process to obtain mutiplets with:

$$j = (j_1 + j_2), (j_1 + j_2 - 1), (j_1 + j_2 - 2), \ldots, |j_1 - j_2|$$

The sequence terminates at $|j_1 - j_2|$, and these are the full set of angular momentum combinations that can arise.

To give more of a sense of how this works, let us look at some examples. The first is the spin case I asked you to keep in mind during the general discussion.

Case: $j_1 = \frac{1}{2}$, $j_2 = \frac{1}{2}$

The possible combinations are

$$j = 1, 0$$

with total multiplicities

$$\sum (2j + 1) = 3 + 1 = 4$$

which fits nicely with

$$(2j_1 + 1) \times (2j_2 + 1) = 2 \times 2 = 4 = 3 + 1 \quad \checkmark$$

Case: $j_1 = 1$**,** $j_2 = \frac{1}{2}$

The possible combinations are

$$j = 3/2, 1/2$$

with total multiplicities

$$\sum(2j+1) = 4 + 2 = 6$$

which fits nicely with

$$(2j_1+1) \times (2j_2+1) = 3 \times 2 = 6 = 4 + 2 \quad \checkmark$$

Case: $j_1 = 1$**,** $j_2 = 1$

The possible combinations are

$$j = 2, 1, 0$$

with total multiplicities

$$\sum(2j+1) = 5 + 3 + 1$$

which fits nicely with

$$(2j_1+1) \times (2j_2+1) = 3 \times 3 = 9 = 5 + 3 + 1 \quad \checkmark$$

Case: $j_1 = 3$**,** $j_2 = 2$

The possible combinations are

$$j = 5, 4, 3, 2, 1$$

with total multiplicities

$$\sum(2j+1) = 11 + 9 + 7 + 5 + 3 = 35$$

which fits nicely with

$$(2j_1+1) \times (2j_2+1) = 7 \times 5 = 35 = 11 + 9 + 7 + 5 + 3 \quad \checkmark$$

Clebsch-Gordon Coefficients

While this gives the general structure for how states $|j_1, m_1\rangle \otimes |j_2, m_2\rangle$ combine into multiplets with total angular momentum $|j, m\rangle$, we have not explicitly calculated the specific coefficients that arise in all cases: how, exactly, do we write $|j, m\rangle$ in terms of the product states?

Unfortunately (or fortunately) there are no easy and simple expressions for these coefficients that you can learn. They are given by what are called *Clebsch-Gordon coefficients* and you can look them up for specific cases if you need to. In particular, we can write

$$|j, m, j_1, j_2\rangle = \sum_{m_1, m_2} C_{j,m,j_1,m_1,j_2,m_2} |j_1, m_1\rangle \otimes |j_2, m_2\rangle. \tag{8.11}$$

That is, the Clebsch-Gordon coefficients C_{j,m,j_1,m_1,j_2,m_2} are the coefficients in the expansion of the $|j, m\rangle$ state present in the composite system of two elements with individual angular momenta j_1 and j_2.

The simplest example of Clebsch-Gordon coefficients is in the composition of two spnin 1/2 particles. For example,

$$|1, 0\rangle = \frac{1}{2} \left(|\frac{1}{2}, \frac{1}{2}\rangle |\frac{1}{2}, -\frac{1}{2}\rangle + |\frac{1}{2}, -\frac{1}{2}\rangle |\frac{1}{2}, \frac{1}{2}\rangle \right) \tag{8.12}$$

and so

$$C_{1,0,1/2,1/2,1/2,-1.2} = C_{1,0,1/2,-1/2,1/2,1.2} = \frac{1}{\sqrt{2}}.$$

Angular Momentum and Magnetic Moments

We now move on to discuss the link (for charged particles) between angular momentum and magnetic moments. Even if you have not explicitly expressed it in this way, the topic should, at least in part, be familiar to you. For example, think back to 1st year electromagnetism where you would have used the Biot-Savart law to show that a small circular loop of current (which clearly carries angular momentum) behaves like a magnetic moment. Thinking about this, it should not be surprising that charged particles with angular momentum carry a magnetic moment.

We want to make this connection more precise. First of all, recall the standard result relating the **B** field to the vector potential **A**,

$$\mathbf{B} = \nabla \times \mathbf{A}.$$

Here we want to start by using a result from classical mechanics about the Hamiltonian for a particle in a magnetic field. If you do the S7 Classical Mechanics option, you may see this result derived (this depends on precisely how that course is lectured). In any case, for the purpose of *this* course, please just accept it as a result that the Hamiltonian for a particle in a magnetic field is

$$H = \frac{(\mathbf{p} - e\mathbf{A})^2}{2m},$$

with $\mathbf{A}$ the vector potential. Expanding this (still classical) expression,

$$H = \frac{p^2}{2m} - \frac{e}{2m}(\mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A}) + \frac{e^2\mathbf{A}^2}{2m}. \tag{8.13}$$

We are going to restrict to the case of weak magnetic fields (the small field limit), in which we can neglect the A^2 term and only keep the linear terms. In this case, we obtain for the Hamiltonian of a charged particle in a weak magnetic field

$$H = \frac{p^2}{2m} - \frac{e}{2m}(\mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A}) \tag{8.14}$$

We want to assume (for simplicity, and for understanding how angular momentum couples to a magnetic field) that the magnetic field is constant or nearly constant. For a constant field, we can write out the vector potential explicitly:

$$\mathbf{A} = \frac{1}{2}\mathbf{B}\times\mathbf{x} \tag{8.15}$$

which expands as:

$$\mathbf{A} = \frac{1}{2}\left(zB_y - yB_z, xB_z - zB_x, yB_x - xB_y\right).$$

You can verify that form of the vector potential generates a constant magnetic field. Substituting in this form for $\mathbf{A}$, we obtain

$$H = \frac{p^2}{2m} - \frac{e}{4m}((\mathbf{B}\times\mathbf{x})\cdot\mathbf{p} + \mathbf{p}\cdot(\mathbf{B}\times\mathbf{x})).$$

Applying the vector identity $\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c}) = \mathbf{b}\cdot(\mathbf{c}\times\mathbf{a}) = \mathbf{c}\cdot(\mathbf{a}\times\mathbf{b})$, this simplifies to:

$$H = \frac{p^2}{2m} - \frac{e}{4m}\left((\mathbf{x}\times\mathbf{p})\cdot\mathbf{B} + \mathbf{B}\cdot(\mathbf{x}\times\mathbf{p})\right),$$

which further reduces to:

$$H = \frac{\mathbf{p}^2}{2m} - \frac{e}{2m}(\mathbf{B}\cdot\mathbf{L}) \tag{8.16}$$

where $\mathbf{L}$ is the orbital angular momentum $\mathbf{L} = \mathbf{x}\times\mathbf{p}$.

From this, we see that the (classical) magnetic moment $\boldsymbol{\mu}$ of a particle with orbital angular momentum $\mathbf{L}$ is given by:

$$\boldsymbol{\mu} = \frac{e}{2m}\mathbf{L}, \tag{8.17}$$

as the Hamiltonian then takes the form:

$$H = -\boldsymbol{\mu}\cdot\mathbf{B}$$

which is the appropriate interaction of a magnetic moment with the magnetic field.

Note that Eq.(8.17) refers to *orbital* angular momentum, $\mathbf{L} = \mathbf{x} \times \mathbf{p}$. To make contact with your future studies of physics, I will rewrite Eq.(8.17) as

$$\boldsymbol{\mu} = \frac{ge}{2m}\mathbf{L}, \tag{8.18}$$

with $g = 1$. This seems odd, but there is method in the oddity and you shall fully understand the significance of this if you study the Dirac equation and understand the magnetic moment associated to the spin of the electron.[6]

Quantum Considerations

The above was a classical expression for the Hamiltonian and the above analysis was *classical*. I will state here (but not fully justify, as any quantum treatment of the electromagnetic field is beyond this course) that this also gives the quantum coupling of a particle to a background electromagnetic field. One point to notice here is that in the classical Hamiltonian, there are times when $\mathbf{x}$ precedes $\mathbf{p}$, and times when $\mathbf{p}$ precedes $\mathbf{x}$ – and we do not worry about this, because this makes no difference in a classical expression.

In a quantum Hamiltonian, the order of operators *does* matter (when they don't commute). How do we know when to turn a classical Hamiltonian

$$H_{class} = AB \tag{8.19}$$

into

$$H_1 = AB \tag{8.20}$$

or

$$H_2 = BA \tag{8.21}$$

or

$$H_3 = 1/2(BA + AB) \tag{8.22}$$

How do we know which one is right?

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[6] Here we shall just state that the coupling of the Dirac equation, the relativistic wave equation for spinors, to electromagnetism leads to $g = 2$ for the electron (quantum electrodynamics generates further small higher-order corrections). It was a historically highly important result to find that the Dirac equation automatically gave $g = 2$ for spin angular momentum whereas $g = 1$ for orbital angular momentum; it was the first strong sign that physicists had a consistent relativistic theory of the electron.

We don't, and ultimately THIS IS THE WRONG QUESTION! The world does *not* go from classical theory to quantum theory. The world goes from quantum theory to classical theory. Instead, we should take a quantum Hamiltonian and explore its consequences (and so decide whether or not this is the right theory). In fact, there are many known examples in physics where the (true) quantum theory looks totally different, in terms of both behaviour and degrees of freedom, than you could possible anticipate by looking at the classical limit.[7]

So even though you will see it done in various places as a heuristic approach, it is *never* correct to infer the equations of motion of a quantum system simply from taking a classical Hamiltonian and promoting it to a quantum one. Rather, we should view this an empirical approach to suggest a suitable Hamiltonian from which we construct predictions and compare with experiment (and it *is* true that the interaction of quantum particles with background magnetic fields is given by Eq. (8.16)).

8.4 Beam Splitting and Stern-Gerlach Experiments

The presence of a term

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}$$

in the Hamiltonian means that, if a particle has a magnetic moment arising from angular momentum, the overall energy of the particle depends on the size of the magnetic field. As with any Hamiltonian, particles 'want' to move to regions of lower energy. This means that if put a slight gradient in the magnetic field, then particles are deflected – and the larger their magnetic moment (angular momentum), the greater the deflection.

This setup is realised in a *Stern-Gerlach* experiment. A beam of particles is sent into a magnetic field with a slight gradient. If the magnetic field is aligned along the z-direction, then the particle beams splits into a number of sub-beams, each determined by the z-component of the angular momentum.

The induced force inside the magnetic field is

$$F = -\frac{\partial V}{\partial z} = \boldsymbol{\mu}_z \frac{\partial B}{\partial z}$$

and so as $\boldsymbol{\mu} \propto \boldsymbol{L}$, the beam is split according to the angular momentum of the particles. Pure beams of fixed m_z value can then be generated by starting with mixed beams and passing them through the Stern-Gerlach experiment.

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[7] One of the best examples of this is the low-energy behaviour of the strong nuclear force. The semi-classical limit is describe by pions, although the underlying quantum degrees of freedom are quarks and gluons which are completely invisible in the classical limit.

Observational Implications

The number of ways the beam splits is given by the number of distinct angular momentum values. If we only had orbital angular momentum (given by the L quantum number), then we would expect the beam to be split in $2L+1 = 1, 3, 5\dots$ ways (corresponding to integer values of angular momentum). However, for electron spin angular momentum the beam is split in $2S + 1 = 2$ ways. The fact that an electron beam is split in two ways inside a Stern-Gehrlach experiment was historically important in understanding the existence and nature of electron spin.

A Stern-Gerlach splitter in the (say) z-direction resolves an originally incoherent beam of electrons into two coherent pure beams, one corresponding to the spin-up $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ state, and the other corresponding to the spin-down $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ state. Stern-Gerlach experiments are useful test cases for quantum measurement, as by passing a beam through Stern-Gerlach splitters oriented along different axes we can project the qauntum state into eigenstates of S_x, S_y, S_z (depending on the precise orientation of the splitter).

8.5 Bell Inequalities

To appear.

9. Hydrogen(ic) Atoms

In this section we study the physics of the basic Hydrogenic atom. 'Basic' means restricted to a system we can solve exactly: this means neglecting all interactions beyond that of the simple Couloumb potential and focusing on a system of a single electron in orbit around a point-like nucleus. This is the simplest and exactly soluble system, and this is what we aim to solve here. We also use the expression 'Hydrogenic' – this refer to the presence of an arbitrarily charged nucleus (i.e. charge $+Ze$ and not just $+e$ as for the proton).

We first look at generalities applicable to spherically symmetric potentials, before gradually narrowing down towards the Hydrogen atom itself.

9.1 Spherically Symmetric Potentials

The Hamiltonian for a particle in a spherically symmetric potential that depends only on the radial coordinate r is

$$H = \frac{\mathbf{p}^2}{2m} + V(r)$$

The bold-face is to make it clear that the momentum operator is in 3 spatial dimensions and so this describes a particle in 3d. As $\mathbf{p}^2 = \mathbf{p} \cdot \mathbf{p}$ is a scalar, this means that the angular momentum operators L^2 and L_z commute with the Hamiltonian:

$$[L^2, H] = [L_z, H] = 0. \tag{9.1}$$

as the radial coordinate:

$$r = \sqrt{x^2 + y^2 + z^2}$$

is also a scalar which remains invariant under rotations.

Recall that the intuition here is that the angular momentum operators correspond to the generators of rotations, and so quantities which are invariant under rotations will commute with the angular momentum operators.

This means that, for spherically symmetric systems, we can always diagonalise energy eigenfunctions in terms of L^2, so that we can write any energy eigenfunction as

$$|n, l, m\rangle \quad \text{(angular momentum quantum numbers)}.$$

Here l and m are the ordinary angular momentum quantum numbers, with $Y_{lm}(\theta, \phi)$ the spherical harmonic, whereas n captures all other quantum numbers. It *is* true that in the Hydrogen atom, then n is the principal quantum number and takes integer values starting at the ground state $n = 1$ and going upwards, but nothing we have done so far tells us this: so far, in terms of general spherically symmetric potential, n just captures 'everything radial'.

In position representation, we can write:

$$\frac{\mathbf{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2$$

which expands in spherical polar coordinates as:

$$\begin{aligned}\frac{\mathbf{p}^2}{2m} &= -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\left(-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\right)\\ &= -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\mathbf{L}^2\right) \qquad (9.2)\end{aligned}$$

The energy eigenfunction equation is (as ever!) $\hat{H}\psi = E\psi$, and so as a differential equation our natural desire is to separate variables. We write

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi), \qquad (9.3)$$

separating out radial and angular degrees of freedom. We then have

$$\nabla^2\psi_{nlm}(r,\theta,\phi) = \left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}R_{nl}(r)\right) - \frac{l(l+1)}{r^2}R_{nl}(r)\right)Y_{lm}(\theta,\phi), \qquad (9.4)$$

using the fact that the eigenvalues of $\mathbf{L}^2$ are $l(l+1)$.

The energy eigenfunction equation now reduces to, for a general potential $V(r)$,

$$-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \left(\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right)R_{nl}(r) = E_{nl}R_{nl}(r), \qquad (9.5)$$

with $Y_{lm}(\theta,\phi)$ having been factored out. For a given form of $V(r)$, we now find the energy eigenfunctions by 'just' solving Eq. 9.5 for $R_{nl}(r)$ and E_{nl}. Note that we can view the $\mathbf{L}^2$ term as contributing a sort of 'centrifugal potential', which increases for higher angular momentum quantum numbers l.

9.2 The Hydrogen Atom

We now do want to specialise down to the actual case of a Hydrogen atom consisting of an orbiting electron bound to a central nucleus through a Coulomb interaction. When doing so, it is important to remember that we are solving a real physical system. So, before going further, let us remind ourselves of the basic physical scales involved in the Hydrogen atom:

- Nuclear radius of around 10^{-15}m.

- Electron orbital radius around 10^{-10}m.
- Typical energy levels around a few electron-Volt (note bound state energies are negative).

Also recall that the general form of the Coulomb potential is

$$V = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r}. \tag{9.6}$$

The Hydrogen(ic) atom has two particles: an electrona and the nucleus, plus a Coulomb interaction between the two. The corresponding Hamiltonian is

$$H = \underbrace{\frac{\mathbf{p}_N^2}{2m_N}}_{\text{Nuclear kinetic energy}} + \underbrace{\frac{\mathbf{p}_e^2}{2m_e}}_{\text{Electron kinetic energy}} - \underbrace{\frac{Ze^2}{4\pi\varepsilon_0|\mathbf{x}_e - \mathbf{x}_N|}}_{\text{Coulomb interaction}}. \tag{9.7}$$

This type of problem is (or at least should be!) familiar from your studies of classical mechanics. Hopefully you instinctively reach for center of mass coordinates and the concept of *reduced mass*, to factorise the problem into the worthy but dull motion of the centre of mass and the far more interesting behaviour of the reduced mass around the centre of mass. The centre of mass coordinate is

$$\mathbf{X} = \frac{m_e \mathbf{x}_e + m_N \mathbf{x}_N}{m_e + m_N}, \tag{9.8}$$

while the displacement from the center of mass is given by

$$\mathbf{r} = \mathbf{x}_e - \mathbf{x}_N. \tag{9.9}$$

We also define the reduced mass

$$\mu = \frac{m_e m_N}{m_e + m_N}, \tag{9.10}$$

and note that if $m_N \to \infty$, then $\mu \to m_e$ (which is the correct behaviour for an infinitely heavy, unmoving central nucleus). Following this change of coordinates (and for the details here I refer you to a classical mechanics course), the Hamiltonian becomes

$$H = \frac{\mathbf{p_X}^2}{2(m_e + M_N)} + \frac{\mathbf{p_r}^2}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r}, \tag{9.11}$$

which is now the sum of the kinetic energy of center of mass, the kinetic energy of the reduced mass and the potential energy. In particular, this Hamiltonian is now *separable*,

$$H_{total} = H(\mathbf{X}) + H(\mathbf{r}),$$

with the Hamiltonian for the center of mass motion being the simple free-particle Hamiltonian

$$H(\mathbf{X}) = \frac{\mathbf{p_X}^2}{2(m_e + M_N)} \tag{9.12}$$

and that for the relative coordinate being

$$H(\mathbf{r}) = \frac{\mathbf{p_r}^2}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r}. \tag{9.13}$$

As this system is nicely separable, we can now factorise the overall wavefunction,

$$\psi(\mathbf{x}_e, \mathbf{x}_N) = \phi(\mathbf{X})\chi(\mathbf{r}). \tag{9.14}$$

$\phi(\mathbf{X})$ satisfies the free particle equation and so has the simple free particle form,

$$\phi(\mathbf{X}) = Ae^{i\mathbf{k}\cdot\mathbf{X}}, \tag{9.15}$$

subject to all the caveats about how to normalise free particle wavefunctions that we discussed earlier in these lectures. Meanwhile, $\chi(\mathbf{r})$ sits in a spherically symmetric potential. We factorise it as

$$\chi(\mathbf{r}) = \chi_{nl}(r)Y_{lm}(\theta, \phi), \tag{9.16}$$

and χ_{nl} then satisfies, as per our earlier discussion around Eq. (9.5),

$$\left(-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \left(\frac{\hbar^2 l(l+1)}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r}\right)\right)\chi_{nl}(r) = E_{nl}\chi_{nl}(r), \tag{9.17}$$

and this is the equation we have to solve.

On one level, this is just a differential equation. Depending on taste and inclination, we can put it into an AI model, enter it into Mathematica, or look up a large textbook with every standard form of differential equations ever dreamed up. The eigenfunctions and eigenvalues of this differential equation duly give us the the eigenfunctions and energy eigenvalues of the harmonic oscillator.

What we aim to do first, though, is gain some understanding of the *form* of the solutions, both in the small-radius and large-radius limits. As ever in physics, *small* and *large* have no absolute meaning, but are only defined relative to a particular scale. In the case of the Hydrogen atom, this scale is the *Bohr radius*,

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}. \tag{9.18}$$

For *Hydrogenic* atoms, the equivalent of the Bohr radius is

$$a_Z = \frac{4\pi\epsilon_0\hbar^2}{\mu Z e^2}, \tag{9.19}$$

where we replace the electron mass by the reduced mass. In terms of these, we define a new dimensionless radial variable,

$$\rho = \frac{r}{a_Z}, \tag{9.20}$$

which define a length scale relative to the (generalised) Bohr radius. Large ρ now specifies large radius and small ρ specifies small radius (and $\rho \sim 1$ corresponds to physics occurring at the (generalised) Bohr radius). In terms of ρ, the differential equation now becomes

$$-\frac{d^2\chi_{nl}(\rho)}{d\rho^2} - \frac{2}{\rho}\frac{d\chi_{nl}(\rho)}{d\rho} + \left(\frac{l(l+1)}{\rho^2} - \frac{2}{\rho}\right)\chi_{nl}(\rho) = E'_{nl}\chi_{nl}(\rho), \tag{9.21}$$

with E'_{nl} related to E_{nl} by

$$E'_{nl} = \frac{2\mu a_Z^2}{\hbar^2}E_{nl}. \tag{9.22}$$

We seek *bound state* solutions, with the electron tied to the nucleus. Bound states have $E'_{nl} < 0$ (recall that the electron at infinity would have zero energy, and so negative energy solutions represent those that cannot escape to infinity: i.e. are bound to the nucleus).

We first consider the behaviour at large values of $\rho \gg 1$. Asymptotically, the leading behaviour is determined by the terms at dominant at large ρ and we can neglect the terms suppressed by powers of ρ in the $\rho \to \infty$ limit. In particular, the terms $\frac{l(l+1)}{\rho^2}\chi_{nl}(\rho)$ and $\frac{2}{\rho}\chi_{nl}(\rho)$ are clearly suppressed compared to $E'_{nl}\chi_{nl}(\rho)$ by itself. If $\chi_{nl}(\rho)$ was power-law in ρ, then we would also see that the derivative terms $\frac{d^2\chi_{nl}(\rho)}{d\rho^2}$ and $\frac{2}{\rho}\frac{d\chi_{nl}(\rho)}{d\rho}$ would be suppressed compared to $E'_{nl}\chi_{nl}(\rho)$ and there would be no solution.

This tells us that the asymptotic form of $\chi_{nl}(\rho)$ should be an exponential. Taking an ansatz

$$\chi_{nl}(\rho) \sim \rho^\alpha e^{-\lambda_{nl}\rho}, \tag{9.23}$$

we see that this solves the leading large-ρ behaviour, provided that $\lambda_{nl}^2 = |E'_{nl}|$.

Having identified the asymptotic large-ρ behaviour, we now consider the small-ρ behaviour. In this case, it is the $\frac{l(l+1)}{\rho^2}\chi_{nl}(\rho)$ term that dominates over the $\frac{2}{\rho}\chi_{nl}(\rho)$ and $E'_{nl}\chi_{nl}(\rho)$ terms, and so our equation becomes (we assume here that $l \neq 0$)

$$-\frac{d^2\chi_{nl}(\rho)}{d\rho^2} - \frac{2}{\rho}\frac{d\chi_{nl}(\rho)}{d\rho} + \frac{l(l+1)}{\rho^2}\chi_{nl}(\rho) = 0. \tag{9.24}$$

Let us try a solution $\chi_{nl}(\rho) \sim \rho^s$. Substituting this in, we get

$$-s(s-1) - 2s + l(l+1) = 0,$$

that is

$$-s(s+1) + l(l+1) = 0, \tag{9.25}$$

which is solved by $s = l$ or $s = -l-1$. The second solution is not normalisable, and so we obtain a small-radius solution

$$\chi_{nl}(\rho) \sim \rho^l, \tag{9.26}$$

for $\rho \ll 1$. In fact this behaviour is also true for $l = 0$, with the leading behaviour near $\rho = 0$ a constant, $\chi_{nl} \sim A$ (in case you are wondering how the powers match, this is completed into an exponential in the full solution).

Having identified the asymptotic behaviour of the eigenfunctions, we now move towards a full solution.

9.3 Full Solution

Given the exponential fall-off at large values of ρ and the power-law behaviour at small values of ρ, a natural ansatz for the full solution is

$$\chi_{nl}(\rho) = \rho^l e^{-\lambda_{nl}\rho} F_{nl}(\rho). \tag{9.27}$$

The aim is to 'pull out' the already-identified behaviour at both small ρ and large ρ, and then use $F_{nl}(\rho)$ to parametrise whatever is left. If we take the form of $\chi_{nl}(\rho)$ from Eq. (9.27) and substitute it into Eq. (9.21), then (after various taking derivatives and gathering terms) we obtain

$$-\rho\frac{d^2F_{nl}(\rho)}{d\rho^2} - 2(l+1-\lambda_{nl}\rho)\frac{dF_{nl}(\rho)}{d\rho} + 2\left(\lambda_{nl}(l+1) - 1\right)F_{nl}(\rho) = 0. \tag{9.28}$$

This is now moving towards the form of a standard differential equation. To put it into this form explicitly, we do one further rescaling, writing

$$y = 2\lambda_{nl}\rho. \tag{9.29}$$

On this rescaling, Eq. (9.28) becomes

$$y\frac{d^2F_{nl}(y)}{dy^2}+\frac{dF_{nl}(y)}{dy}\left(2l+2-y\right)+\left(\frac{1}{\lambda_{nl}}-l-1\right)F_{nl}(y)=0. \tag{9.30}$$

This now takes the form of the *generalised Laguerre equation* (you will have studied the Laguerre equation itself in the Mathematical Methods course). The *generalised Laguerre equation* takes the form

$$y\frac{d^2f(y)}{dy^2}+\frac{df(y)}{dy}\left(\alpha+1-y\right)+kf(y)=0, \tag{9.31}$$

with α an arbitrary real number. Non-singular solutions occur when k is a non-negative integer (and recall here that k is related to the eigenvalue, and so this condition turns into the quantisation condition for the eigenvalue: the eigenvalues are fixed by requiring they produce non-negative integer k). The solutions are the *generalised Laguerre polynomials* $L_k^{(\alpha)}(y)$.

In our case, we have

$$\alpha=2l+1$$

and

$$k=\frac{1}{\lambda_{nl}}-l-1.$$

The quantisation condition of Laguerre's equation imposes that

$$k=\frac{1}{\lambda_{nl}}-l-1\in\mathbb{Z}\geq 0. \tag{9.32}$$

We therefore see that, in terms of possible solutions for λ_{nl}, we have

- $l=0$, $\frac{1}{\lambda_{nl}}=1,2,3,4$
- $l=1$, $\frac{1}{\lambda_{nl}}=2,3,4$
- $l=2$, $\frac{1}{\lambda_{nl}}=3,4$

and the explicit forms of the (radial) wavefunctions are given by

$$\chi_{nl}(r)=N_{nl}r^lL_{n-l-1}^{(2l+1)}\left(2r/na_z\right)e^{-r/na_Z}, \tag{9.33}$$

where N_{nl} is fixed by the requirement that the overall wavefunction be normalised (which, recall, also includes the angular dependence through the spherical harmonics).

The full wavefunction is then given by

$$\chi(\mathbf{r}) = N_{nl} r^l L_{n-l-1}^{(2l+1)}\left(2r/na_z\right) e^{-r/na_Z} Y_{lm}(\theta, \phi). \tag{9.34}$$

Associated to this, we have *three* quantum numbers. The quantisation condition of Eq. (9.32) implies that $\lambda_{nl} = 1/n$ with $n \in \mathbb{Z}$. The quantum numbers are then

- n is the *principal quantum number*. It runs $n = 1, 2, 3, \ldots$. As we shall very shortly see, it indexes the energy levels of the atom.
- l measures the *total* orbital angular momentum of the electron (in this treatment we are neglecting the electron spin and its role in angular momentum). It is can take values $0 \leq l \leq n-1$.
- m measures the z-component of angular momentum. It has a range $-l \leq m \leq l$ which it moves through in integer units.

In terms of the energy levels, the quantisation condition for solutions to exist was

$$\lambda_{nl} = \frac{1}{n}. \tag{9.35}$$

This corresponds to

$$E'_{nl} = \frac{1}{n^2} \tag{9.36}$$

and so

$$\begin{aligned} E_{nl} &= -\frac{\hbar^2}{2\mu a_z^2}\frac{1}{n^2} \qquad (9.37)\\ &= -\frac{\mu e^4 Z^2}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} \qquad (9.38)\\ &= -\left(\frac{\mu}{m_e}\right) Z^2 \frac{E_R}{n^2}, \qquad (9.39) \end{aligned}$$

where

$$E_R = \frac{m_e e^4}{32\pi^2\epsilon_0^2\hbar^2} = 13.6\text{eV} \tag{9.40}$$

is called the *Rydberg constant* and is one of these values that you ought simply to remember and not forget: it is the core energy value of atoms that you need to know.

Note that the energy levels depend only on n; there is no dependence on the angular momentum quantum number l. This is a slightly surprising feature, as these wavefunctions are physically quite different: higher-l wavefunctions are further displaced from the origin, and so it surprising that we find exact degeneracy between wavefunctions of the same value of n but different values of l.

In fact, this exact degeneracy only holds at lowest order: all higher-order effects do become sensitive to the differing l values, and so there does end up being some splitting between wavefunctions with the same value of n and differing values of l.

Of course, we do not (directly or easily) observe energy eigenvalues and eigenfunctions. What we most easily observe are transitions between energy eigenfunctions, when an atom falls from one energy level to another and emits a photon while doing so.[8] The result is the emission of a photon with energy

$$E_\gamma = E_1 - E_2 = \left(\frac{\mu}{m_e}\right) Z^2 E_R \left(\frac{1}{n^2} - \frac{1}{m^2}\right), \tag{9.41}$$

for an atom falling from the mth state to the nth state. One particularly important example of such a transition is the Kα line in Hydrogen, coming from transition from a $2p$ ($m = 2$) state to a $1s$ ($n = 1$) state.

Certain types of transitions come with certain names. The *Lyman* series refers to the transitions to $n = 1$ states, namely $2 \to 1$, $3 \to 1$, $4 \to 1$ etc transitions. The energy levels in the Lyman sequence are

$$E_\gamma = E_1 - E_2 = \left(\frac{\mu}{m_e}\right) Z^2 E_R \left(1 - \frac{1}{m^2}\right), \tag{9.42}$$

The Balmer sequence refers to transitions to $n = 2$ states, namely $3 \to 2$, $4 \to 2$, $5 \to 2$ etc transitions. The energy levels in the Balmer sequence are

$$E_\gamma = E_1 - E_2 = \left(\frac{\mu}{m_e}\right) Z^2 E_R \left(\frac{1}{4} - \frac{1}{m^2}\right). \tag{9.43}$$

The Paschen sequence refers to transitions to $n = 3$ states, namely $4 \to 3$, $5 \to 3$, $6 \to 3$ etc transitions. The energy levels in the Paschen sequence are

$$E_\gamma = E_1 - E_2 = \left(\frac{\mu}{m_e}\right) Z^2 E_R \left(\frac{1}{9} - \frac{1}{m^2}\right). \tag{9.44}$$

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[8] But – I hear you object – energy eigenfunctions are stationary states and so should remain as such forever, rather than being able to decaying from one higher energy state to another lower energy state. Well, in practice all things decay; ‘The woods decay, the woods decay and fall // The vapours weep their burthen to the ground, // Man comes and tills the field and lies beneath, // And after many a summer dies the swan.’(Tennyson) The real world is not an idealised system; how this arises in practice is that when we couple to electromagnetism then all these eigenstates become only *approximate* rather than exact stationary states – they slowly decay through emission of a photon.

We should also note here the overall degeneracies of the energy levels. Based on the above analysis, the energy level n has l values running from 0 to $n-1$, and each l value has $2l+1$ m values. Putting this together, we find that the total degeneracy of the nth level is

- The $n = 1$ level is 1-fold degenerate
- The $n = 2$ level is (1 + 3)-fold degenerate, namely 4-fold degenerate
- The $n = 3$ level is (1 + 3 + 5)-fold degenerate, namely 9-fold degenerate
- In general, the nth level is n^2-degenerate.

Note that when we include the internal electron spin states, then these degeneracies all double (as, in addition to the position wavefunction, the electron can then *also* be in either the spin-up state or the spin-down state, which are both distinct – doubling the number of states present at each energy level).

In the context of chemistry and atomic structure, the $l = 0$, $l = 1$, $l = 2$, $l = 3$ states are all often called s, p, d and f states – please be aware of this notation as you connect the analysis here to your broader knowledge and also other books you might read.

We also state here the explicit forms of some of the lowest wavefunctions (ground state $n = 1$ and first excited state $n = 2, l = 0, 1$). We have

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a_Z^3}} e^{-r/a_Z}, \tag{9.45}$$

$$\psi_{200}(r,\theta,\phi) = \frac{1}{\sqrt{8\pi a_Z^3}} \left(1 - \frac{r}{2a_Z}\right) e^{-r/2a_Z}, \tag{9.46}$$

$$\psi_{211}(r,\theta,\phi) = -\frac{1}{8\sqrt{\pi a_Z^3}} \frac{r}{a_Z} e^{-r/2a_Z} \sin\theta e^{i\phi}, \tag{9.47}$$

$$\psi_{210}(r,\theta,\phi) = -\frac{1}{4\sqrt{2\pi a_Z^3}} \frac{r}{a_Z} e^{-r/2a_Z} \cos\theta, \tag{9.48}$$

$$\psi_{21-1}(r,\theta,\phi) = \frac{1}{8\sqrt{\pi a_Z^3}} \frac{r}{a_Z} e^{-r/2a_Z} \sin\theta e^{-i\phi}. \tag{9.49}$$

Note that overall phases in these wavefunctions are purely conventional and do not carry physical significance.

Also note, as previously discussed, the way in which the $l = 1$ wavefunctions vanish at the origin: in terms of classical intuition, you can imagine the electron with non-zero angular momentum being ‘thrown outwards’, when viewed in terms of centrifugal forces and so always found away from the exact origin.